THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Hydrogen Production with Carbon Dioxide Capture by Reforming of Natural Gas using Chemical-Looping Technologies

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Department of Energy and Environment
Chalmers University of Technology
Göteborg, Sweden, 2006

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ABSTRACT

Two novel processes for H_2 production by reforming of fossil fuels with CO_2 capture are examined. Both processes utilize the principles of chemical-looping combustion, which is an innovative combustion technology that can be used for CO_2 capture in power generating processes. In chemical-looping combustion, direct contact between fuel and combustion air is avoided. Instead, a solid oxygen carrier performs the task of bringing oxygen from the air to the fuel. Thus, the resulting CO_2 is not diluted with N_2 and can easily be recovered.

Chemical-looping reforming is basically a process for partial oxidation of hydrocarbon fuel, where chemical looping is used as a source of undiluted oxygen. Chemical-looping reforming has been demonstrated in a laboratory reactor consisting of two interconnected fluidized beds. Particles of NiO and $MgAl_2O_4$ were used as bed material and oxygen carrier. Natural gas was used as fuel. The reactor temperature was 820-930 ºC. In the fuel reactor the oxygen carrier was reduced by the fuel, which in turn was partially oxidized to H_2, CO, CO_2 and H_2O. In the air reactor the oxygen carrier was reoxidized with air. H_2 production by chemical-looping reforming with CO_2 capture has also been examined in a process study in which it was found that an overall reformer efficiency of 81%, including CO_2 capture and CO_2 compression, is possible. To obtain such high efficiency the whole system would need to be pressurized and integrated with a gas turbine.

Steam reforming of natural gas with CO_2 capture by chemical-looping combustion resembles conventional steam reforming, but the reformer furnace is replaced by chemical-looping combustion. Instead, reforming takes place in reactor tubes located inside the chemical looping fuel reactor. Energy for the endothermic reforming reactions is provided by fluidized bed heat exchange. Steam reforming with CO_2 capture by chemical-looping combustion has been examined in a process study. It was found that CO_2 for sequestration could be obtained without efficiency penalty and that the selectivity for H_2 could be improved compared to conventional steam reforming due to low reactor temperature and more favorable heat-transfer conditions. The overall reformer efficiency could be 80% or higher, including CO_2 capture and CO_2 compression. Additionally, a model describing one single reformer tube surrounded by a fluidized bed was made to check the feasibility of the concept. The two models were combined and used to make a tentative reactor design. Reactor dimensions, particle flows, gas flows, pressure drops, heat transfer operations and temperature levels all seemed reasonable.

Keywords: Chemical-looping reforming, chemical-looping combustion, steam reforming, partial oxidation, hydrogen, synthesis gas, carbon sequestration

LIST OF PUBLICATIONS

This licentiate thesis is based on the following papers, referred to by roman numbers in the text:

I. Rydén M, Lyngfelt A. Hydrogen and power production with integrated carbon dioxide capture by chemical-looping reforming. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, September 2004.

II. Rydén M, Lyngfelt A. Using steam reforming to produce hydrogen with carbon dioxide capture by chemical-looping combustion. International Journal of Hydrogen Energy, in press, available online 26 January 2006.

III. Rydén M, Lyngfelt A, Mattisson T. Synthesis gas generation by chemical-looping reforming in a continuously operating laboratory reactor. Fuel, in press, available online 10 March 2006.

Contribution by the author:

I. Principal author, responsible for modelling, data evaluation and writing.
II. Principal author, responsible for modelling, data evaluation and writing.
III. Principal author, responsible for experimental work, data evaluation and writing.

Related publications not included in the thesis:

- Rydén M. Hydrogen production by reforming of natural gas with carbon dioxide capture by chemical-looping combustion. Proceedings of the 4th Nordic Minisymposium on Carbon Dioxide Capture, Espoo, Finland, September 2005.

- Abad A, Mattisson T, Lyngfelt A, Rydén M. Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier. Fuel, v 85, p 1174-1185, 2006.

- Rydén M, Lyngfelt A, Mattisson T. Two novel approaches for hydrogen production; chemical-looping reforming and steam reforming with carbon dioxide capture by chemical-looping combustion. Proceedings of the 16th World Hydrogen Energy Conference, Lyon, France, June 2006.

- Rydén M, Lyngfelt A, Mattisson T. Production of H_2 and synthesis gas by chemical-looping reforming. Proceedings of the the 8th International Conference on Greenhouse Gas Control Technologies, Trondheim, Norway, June 2006.

CONTENTS

1. INTRODUCTION

1.1 The greenhouse effect and global warming

In 1827 the French mathematician Joseph Fourier wrote an essay where he summarized his thoughts about the temperature of the earth [1]. In this essay he introduced the idea that certain gases in the atmosphere exerts a thermal blanketing that keeps the planets surface warmer than it otherwise would be. The heating effect that these gases have on our planet has become known as the greenhouse effect and the gases as greenhouse gases. The greenhouse effect can be visualized by a simplified energy balance of the earth surface, see figure 1.

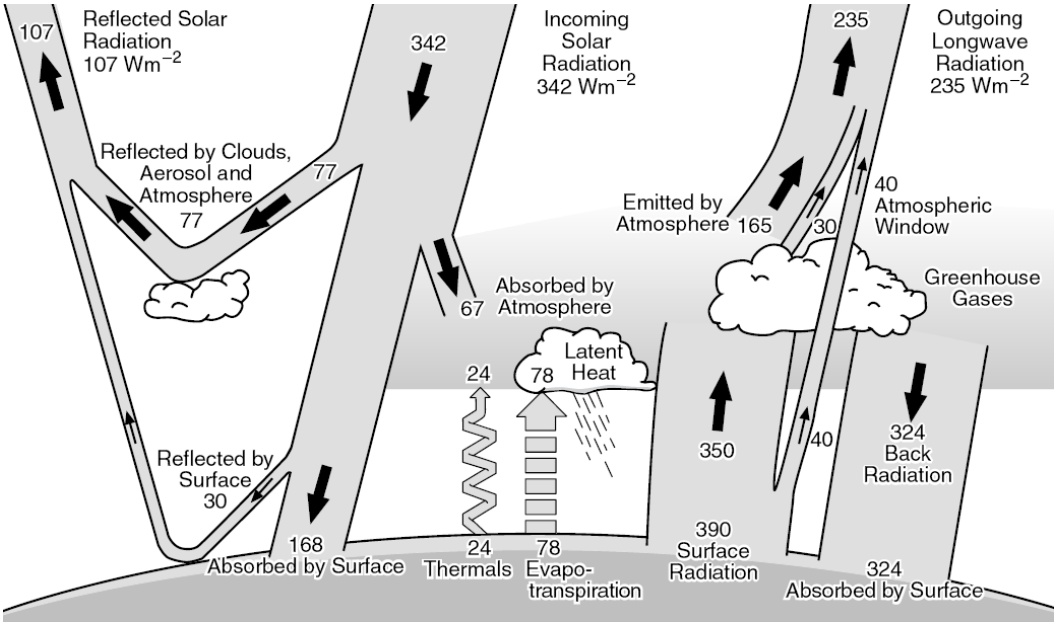


Figure 1. The energy balance of the earth. About half of the incoming solar radiation passes through the clouds and the atmosphere and is absorbed by the surface. Parts of the resulting heat is reflected back as thermal infrared radiation, which in turn is absorbed and scattered by greenhouse gases in the atmosphere and causes the greenhouse effect. IPCC [2].

Science has come far the past 179 years. Today we know that the greenhouse effect is vital to the earth's climate system. At present, it boosts the temperature of our planet about 33 ºC. Without it our world would have been much colder, perhaps even incapable to harbour advanced life forms such as ourselves. It is easily realized that if the concentration of greenhouse gases in the atmosphere is altered, so is the greenhouse effect. Eventually this will have impact on the climate of our planet as well.

The two most important greenhouse gases are water vapour and CO_2. This has been known since 1861, when the British natural philosopher James Tyndall presented experiments that demonstrated the absorbing properties of these gases [3]. Human activities are not believed to influence the concentration of water vapour in the atmosphere directly, but that is not the case for CO_2. It is a well established fact that our way of living is increasing the concentration of CO_2 in the atmosphere rapidly.

In prehistoric times the CO_2 concentration in the atmosphere was much higher than today. The climate was hotter too. By the time when the dinosaurs walked the earth even the arctic areas of our planet were covered with dazzling jungles. Since those days CO_2 has been removed from the atmosphere. The carbon has not just disappeared though. Vast amounts can be found solved in the oceans, bound in minerals and in other so called carbon reservoirs. Transportation of CO_2 from the atmosphere to these kinds of reservoirs is naturally occurring but very slow. The process has been going on for millions of years.

One important carbon reservoir that was built up during prehistoric times is the so called fossil fuels which include oil, coal and natural gas. It is generally believed that fossil fuels are dead organisms that have been transformed into various carbon compounds by age, heat and pressure. When fossil fuels are burnt, carbon that has been stored in the earth's crust for millions of years is suddenly released to the atmosphere as CO_2. Because of the long residual time of CO_2 in the atmosphere, this results in increased atmospheric CO_2 concentration.

Almost all activities associated with our modern societies are dependent on fossil fuels. They are used for production of vehicle fuels, for generation of electricity, as raw material in industrial processes, for household heating, for production of fertilizers

to the agriculture sector and for many other applications. Well over 80% of the primary energy consumption of the world comes from combustion of oil, coal and natural gas. Without these fuels, industrialization as we know it would never have happened.

It took until 1896 before the greenhouse effect was linked to combustion of fossil fuels. This year the Swedish chemist Svante Arrhenius published his famous article *On the influence of carbonic acid in the air upon the temperature of the ground* [4], in which he argues that the concentration of CO_2 in the atmosphere has a strong influence on the climate of the earth. His theory was immediately questioned, but Arrhenius defended his work vigorously and eventually his theories were accepted. Arrhenius was not an alarmist. He even argued in favour of increased CO_2 emissions. In his book *Worlds in the making* [5] from 1908 he suggested that human emission of CO_2 could prevent the world from entering a new ice age, and that a warmer planet would be necessary to feed the rapidly increasing world population. Arrhenius was awarded with the Nobel prize of Chemistry in 1903, and it is a curious incident that the receiver of the prize in 1920, the highly respected German scientist Walter Nernst, had similar ideas. It is said that Nernst even fantasized about setting fire to coal seams in order to release CO_2 for rapid warming of the Earth!

Today, 100 years later, an overwhelming majority of the scientific community comes to a totally different conclusion. From a geological point of view, extraction and combustion of fossil fuels is an incredibly rapid process. It has only been going on for a little more than hundred years and if nothing is done our once gargantuan stockpile of oil and natural gas may very well be history in another hundred years or so. This would lead to a dramatic increase of the CO_2 concentration in the atmosphere which could result in disastrous effects on the climate of the earth. Arrhenius thought that a doubling of the atmospheric CO_2 should take 3000 years. At present, it seems like it will only take a few more decades.

Since 1958, direct measurements of CO_2 in the atmosphere are done on regular basis. In later years, data for the times before the industrial revolution have been estimated, for example by measuring the CO_2 concentration in air trapped in glacier

ice cores. Hence we know for certain that the CO_2 concentration in the atmosphere has increased about 30% since the beginning of the industrial revolution, see figure 2.

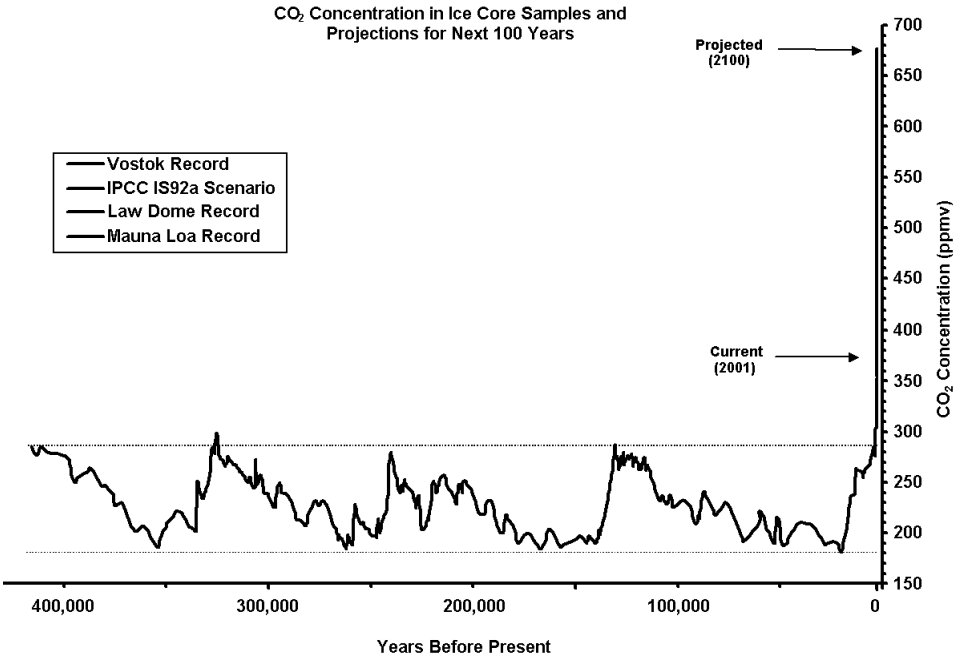


Figure 2. Atmospheric CO_2 concentration for the past 420 000 years estimated by measurements in ice core samples from the Vostok research station at Antarctica, combined with current measurements and a conservative projection for year 2100. Adapted from IPCC [2].

Temperature and precipitation have been carefully monitored for centuries. Therefore we know that the average global surface temperature of our planet has increased at least a half degree centigrade since the beginning of the industrial era, see figure 3 below. A half degree might not sound like a big deal but the temperature of the earth is actually believed to be warmer today than it has been for several thousand years.

Temperature can be estimated by measuring the occurrence of various temperature dependent isotopes present in the air. Hence ice core samples provide information not only about past atmospheric CO_2 concentrations, but information about the climate history of the earth as well. Therefore we know that there is indeed a strong correlation between the CO_2 concentrations in the atmosphere and the climate, see figure 4 below.

There is still some debate about who is the chicken and who is the egg in the correlation between CO_2 and climate, but the general consensus among climatologists is that increased CO_2 concentrations in the atmosphere has an actual heating effect on our planet.

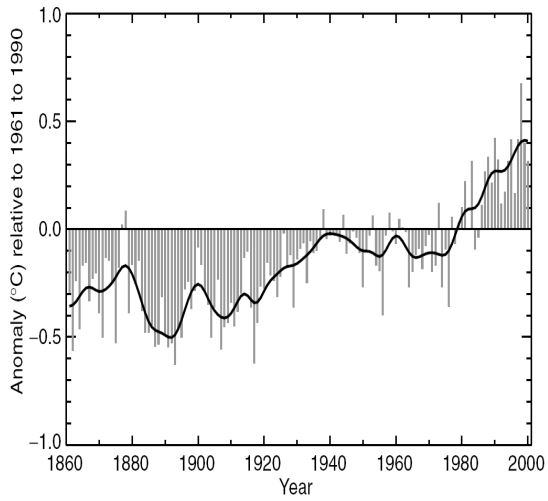


Figure 3. Annual anomalies of global land-surface air temperature, average for the northern and southern hemispheres with the period between 1961 and 1990 used as reference. IPCC [2].

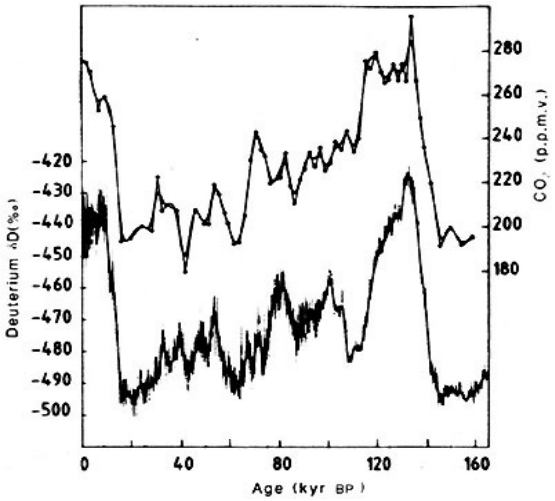


Figure 4. Atmospheric concentrations of CO_2 (upper curve) and the temperature dependent isotope Deuterium (lower curve) plotted against age, expressed as thousands of years before present. From Barnola et al [6].

In later years, concerns that this so called global warming might lead to changes in the climate of the earth have been growing steadily. This is hardly surprising. The prospects are really gloomy. There is little doubt that a sudden increase in the global average temperature with a few degrees would have disastrous consequences, both on the economy and on the ecology of our dear planet. To stop this unsettling development, global CO_2 emissions would need to be reduced greatly in the near future. This is a huge task, to say the least. Whether we like it or not our current dependence on fossil fuels can hardly be overestimated.

A good source for more information about global warming is the IPCC report from 2001, especially the part about the scientific basis [2].

1.2 Ways to reduce anthropogenic CO_2 emissions

Despite the size of the challenge there are plenty of options available to decrease global CO_2 emissions. A comprehensive review can be found in the IPPC report from 2001, especially the part about mitigation [2]. Extensive information about different energy sources can be found in the International Energy Agency report from 2004 [7]. The most frequently discussed options to reduce CO_2 emissions are summarized below:

- ***Reduce global energy consumption***
  If the total energy consumption of the world is reduced, so is the need to burn fossil fuels. This could be achieved either by improved energy efficiency or by a general decrease of power-demanding conveniences. While both these options are possible, reduced energy consumption in the future seems rather unlikely. Historically, energy consumption per capita has been correlated to the general economic development, which is rising steadily on a global scale. The world's population is also increasing. Still, there is no doubt that reduction of careless energy use and construction of an efficient energy infrastructure is a rational start to limit CO_2 emissions.

- ***Increase the use of renewable energy sources***
  Renewable energy sources produce no net CO_2 emissions. Unfortunately, replacing fossil fuels with renewable energy is a gigantic task. Most rivers suitable for hydro power are already developed. Production of various kinds of biofuels is technically possible, but limited by lack of fertile farm land and fresh water resources. Wind power and solar power has big potential but still have some way to go until they will become serious players on the global energy market.

- ***Increase the use of nuclear power***
  Nuclear power produces no CO_2 emissions. The future of nuclear power looks

quite uncertain though. Historically, the private sector has showed modest interest in building nuclear power plants. The risk for weapon proliferation, the problematic waste disposal, shaky public acceptance and juridical limbo are other obstacles surrounding nuclear power. In addition to this, commercially viable deposits of nuclear fuel are highly limited. The later could change if the price of nuclear fuel was increased. It is also possible to improve fuel utilization by nuclear breeding, or by improving the processing of depleted fuel. Both these options are controversial though.

- ***Switch to less carbon intensive fuels***

  If coal is replaced by oil or natural gas the CO_2 emissions per unit produced energy decrease. Coal is said to be more carbon intense than oil and natural gas. Hence fuel switch can be used to temporary reduce CO_2 emissions. The problem is that known deposits of oil and natural gas are limited and strained, while there are immense amounts of coal available at low cost. So in medium or long term, fuel switch does not seem like a viable strategy.

- ***Enhance CO_2 uptake in biomass***

  Through photosynthesis growing plants consume atmospheric CO_2. The CO_2 is converted to various carbon containing compounds building up biomass. If the total amount of biomass on the earth were increased, considerable amounts CO_2 would be drained from the atmosphere. This could be done for example by growing forests in deserts and agric lands or perhaps by stimulating the growths of green algae in the oceans. At present, the exact opposite is happening. In many parts of the world old forests are cut down for wood and farmland, and thus contribute to increased CO_2 concentration in the atmosphere.

- ***CO_2 capture and storage***

  This thesis deals with technologies that can be used for CO_2 capture and storage, which is presented in section 1.3 below.

1.3 An introduction to CO_2 capture and storage

If CO_2 is captured in flue gases from fossil fuel combustion and prevented from reaching the atmosphere it will not contribute to the greenhouse effect. Hence fossil fuels could be used without impact on the climate. The concept is often referred to as carbon sequestration and has received much interest in later years. Unlike most of the options presented in section 1.2 above, CO_2 capture and storage has potential to have real impact on the global CO_2 emissions even in a relatively near future. A useful source for information about carbon sequestration is IPCC:s special report on CO_2 capture and storage [8]. The subject has also been reviewed quite recently by Yamasaki [9] and Anderson et al [10].

Carbon sequestration will require CO_2 capture, CO_2 transportation and CO_2 storage. Basic technologies for all these operations are already commercially available. The current status of experience is briefly presented below:

- ***CO_2 capture***

  Industrial scale CO_2 capture has been practiced for over 80 years. The aim has usually been purification of natural gas or synthesis gas. The most used method has been physical or chemical absorption, which involves scrubbing of the CO_2 containing gas with a liquid solvent. Physical absorption means that CO_2 is solved in the absorbing liquid at high pressure. Chemical absorption means that CO_2 reacts actively with the solvent and forms a weak chemical bond. The CO_2 rich solvent is regenerated by reduced pressure or increased temperature, and high purity CO_2 is released. This kind of technology can be used to capture CO_2 in flue gases from combustion. The concept is usually referred to as *post combustion CO_2 capture*. Another option is to produce H_2 by reforming of fossil fuels and capture CO_2 within the process, where CO_2 often is available at higher partial pressure than in flue gas. Combustion of H_2 produces only H_2O as waste so H_2 can be used for energy production without CO_2 emissions, see section 1.4 below. This concept is called *pre-combustion CO_2 capture*. Chemical-looping reforming, which is described in section 2.5 below, could be

used for pre-combustion CO_2 capture. A third option is to replace the combustion air (O_2/N_2) in a power generating process with pure O_2 and recirculated flue gas ($O_2/H_2O/CO_2$). Hence flue gas without N_2 is obtained and cooling in a condenser is sufficient to obtain pure CO_2. This concept is usually referred to as *oxyfuel combustion*. Chemical-looping combustion, which is described in section 2.4 below, is a variant of the oxyfuel concept that does not require pure O_2. It is also possible to capture CO_2 within industrial processes. A reason to do so could be that CO_2 may be present at high partial pressure, which makes CO_2 capture by absorption comparably straightforward. A summary of available concepts for large scale CO_2 capture can be found in figure 5.

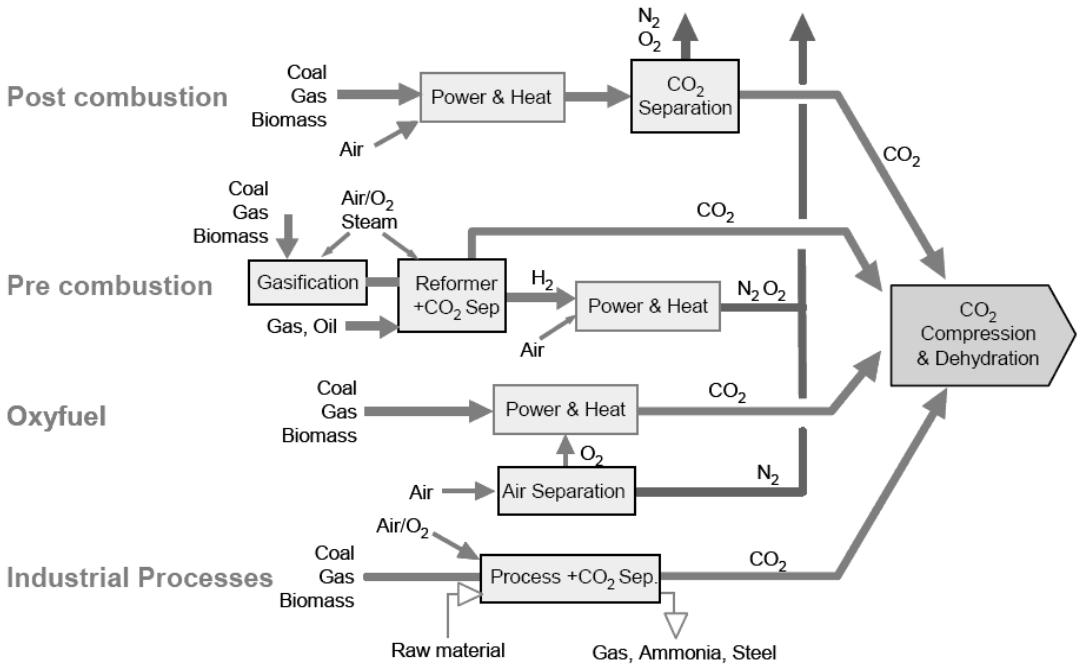


Figure 5: Possible routes for large scale CO_2 capture. IPCC [8].

- ***CO_2 transportation***

  Large scale transportation of CO_2 is nothing new. In western United States there is over 2500 km pipeline that transports over 50 million tons CO_2 annually [8]. This is done to provide CO_2 for enhanced oil recovery. Most of these pipelines have been operated for decades without any major obstacles. Pipeline transport could be complemented by sea transport. At present there is

limited experience with ships for CO_2 transportation, but there should be no major technical barriers for sea transport.

- ***CO_2 storage***

  There are several options available for CO_2 storage. At present, geological storage seems to be the front runner. Geological storage means that CO_2 is returned to where it came from, that is back into the earth crust. Such technology has been practiced at industrial scale for decades. Huge amounts of CO_2 have been pumped into nearly depleted oil fields in order to boost oil production in a procedure called enhanced oil recovery. Similar technology could be used to store CO_2 in depleted oil and gas fields, deep coal beds or saline aquifers. A few existing projects about geological storage will be briefly introduced below. Alternatives to geological storage include ocean storage and mineral carbonation. Ocean storage means that CO_2 is dissolved in ocean water, or stored as homogenous lakes of liquid CO_2 at the sea floor more than 3000 meters below the surface. At present, there are serious concerns about how ocean storage would affect the marine environment and the concept needs further study. Mineral carbonation means that CO_2 is allowed to react with rocks containing for example magnesium oxides, and in some way mimics the natural weathering process. Under most circumstances such reactions are slow and the logistics would involve huge amounts of minerals, but if these problems could be solved mineral carbonation would be a way to bind CO_2 in a harmless form that is guaranteed to last for millenniums to come.

It can be concluded that carbon sequestration does not necessarily require new and fancy technology. Most of the required tools are known and commercially available. This does not mean that carbon sequestration will be for free. The main cost will likely be associated with the capture of CO_2, while transport and storage probably will be less costly.

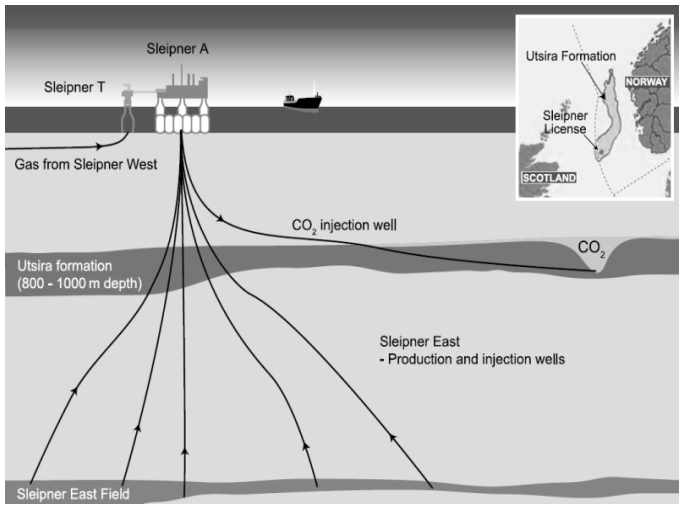
The main alternative for post combustion CO_2 capture and pre-combustion CO_2 capture is absorption. This will require separate absorption facilities which will

increase investment costs. In addition to this, there is a substantial energy demand for regeneration of absorbing solvents such as amines. Oxyfuel combustion requires pure O_2, which is both capital intensive and power demanding to produce. Therefore it is of great interest to develop cheap and efficient technologies for CO_2 capture. Chemical-looping combustion, which is a variant of the oxyfuel concept that is described in section 2.4, does not require pure O_2 and may be a way to capture CO_2 at low cost.

There are several carbon sequestration projects throughout the world that provides valuable knowledge and experience for future developments. Most of them are at modest scale, but there are some notable exceptions that are listed below:

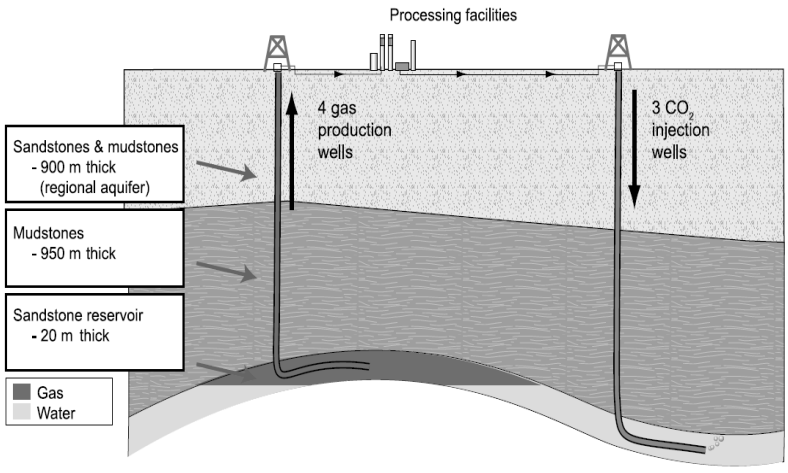
- ***The Sleipner CO_2 storage project***

  At the Sleipner gas field in the North Sea, natural gas is cleaned of 1 million tons CO_2 per year by absorption. The CO_2 is injected into the Utsira formation, which is a deep saline aquifer located 800-1000 meters below the sea floor. The development has been carefully monitored since the start 1996 [8].



- ***The In Shala gas project***

  At the Krechba gas field in Algeria, 1.2 million tons of CO_2 annually is captured from natural gas and injected into water-filled parts of the gas reservoir. Injection started 2004 [8].



- ***Other projects***

  In addition to these two large scale carbon sequestration projects, over 100 million tons of CO_2 is injected into oil wells for enhanced oil recovery each year. Much of this CO_2 is extracted from naturally occurring CO_2 reservoirs, but about 6.5 million ton CO_2/year is captured from natural gas and about 7 million ton CO_2/year is captured from synthesis gas production [8].

1.4 The use of H_2 as carbon free energy carrier

Carbon sequestration has potential to greatly reduce CO_2 emissions from large point sources such as power plants and industries. However, for some applications this kind of technology will not be feasible. It is difficult to imagine CO_2 capture applications for small mobile emission sources such as cars, trucks and airplanes. This is noteworthy since the transportation sector is responsible for almost 25% of the global CO_2 emissions, and this share is increasing.

There is an interesting opportunity to address this problem that could prove to be positive for other sectors of the society as well. Fossil fuels can be converted into H_2, which is an energy carrier that does not contain carbon. Combustion of H_2 produces only H_2O as waste product. If fossil fuels are converted to H_2, and the resulting CO_2 is sequestrated, an energy carrier that can be utilized without greenhouse gas emissions is obtained.

H_2 is a versatile energy carrier. It can be transported and stored in many ways. It can be utilized as it is or in mixture with other gaseous fuels. It should be possible to use H_2 as fuel both in gas turbines and combustion engines. H_2 is also the ideal fuel in most types of fuel cells, which are applications that promises much higher efficiencies than conventional engines. In recent years several prototype vehicles using H_2 in fuels cells as propellant has been taking on the streets of European, Japanese and North American cities, see for example Alvfors et al [11] and Larkins et al [12]. It could also be mentioned that Iceland, a highly developed nation with about 300 000 inhabitants and 180 000 vehicles, has made the move from petroleum-based fuels to H_2 official

policy, see Maack et al [13]. The world's first commercial H_2 station opened in Reykjavík April 24, 2003.

An infrastructure where H_2 is used as the major energy carrier would provide many advantages. Fuel cell vehicles would improve the air quality in cities tremendously since they produce no harmful emissions such as soot, particles, hydrocarbons, NO_X or SO_X. H_2 could also be useful to improve energy security since it can be produced from a wide range of energy sources. H_2 can be produced for example by reforming of fossil fuels, by gasification of biomass or by electrolysis of H_2O with electricity from wind, solar, hydro or nuclear power. The prospects for building an energy infrastructure with H_2 as energy carrier have been reviewed by Ogden [14], and more recently by Khare et al [15].

1.5 The aim of this work

The research presented here deals with H_2 production from natural gas with CO_2 sequestration. Although this route for H_2 might seem less attractive than production from truly sustainable energy sources it has two advantages. Firstly, H_2 production from natural gas and other fossil fuels is proven technology that has been practiced for decades. Secondly, H_2 from fossil fuels will most likely be less costly than H_2 from renewable energy sources, at least in short and medium term. These two factors could be important to obtain public, political and corporate acceptance for H_2 as energy carrier.

It shall also be pointed out that the research presented in this paper can be relevant for other applications than for H_2 production. Reforming of fossil fuels to synthesis gas is an important process within the petrochemical industry. H_2 could also be used directly as fuel in power plants for generation of CO_2 free electricity. The ideas and experiments presented in this thesis have features that make them highly interesting for such applications as well.

2. TECHNICAL BACKGROUND

2.1 Synthesis gas generation

The gaseous mixture of H_2 and CO is usually referred to as synthesis gas. It is an important product that has many uses, for example as feedstock for production of ammonia, methanol and synthetic fuels.

Synthesis gas can be produced from all kinds of fossil fuels. Steam reforming, reaction (1), is suitable for reforming of light fuels such as natural gas. Partial oxidation, reaction (2), can be used for heavier fuels such as oil or coal. CO_2 reforming, reaction (3), can be used if synthesis gas with high CO content is wanted.

Steam reforming:	$C_nH_m + nH_2O \rightarrow nCO + (n+½m)H_2$	(1)
Partial oxidation:	$C_nH_m + (½n)O_2 \rightarrow nCO + (½m)H_2$	(2)
CO_2 reforming:	$C_nH_m + nCO_2 \rightarrow (2n)CO + (½m)H_2$	(3)

At present, the most important method for synthesis gas generation is catalytic steam reforming of natural gas, where reforming takes place in reactor tubes packed with catalyst. Generally, the temperature of reforming is 700-950 ºC and the pressure is 15-40 bar. The tubes are placed inside a furnace and energy for the strongly endothermic reaction (1) is provided by direct firing.

Partial oxidation is slightly exothermic and has typically been used for gasification of coal. An obvious drawback with partial oxidation is that pure O_2 is needed; otherwise produced synthesis gas will be diluted with N_2.

It is possible to design reactor systems that combine endothermic steam reforming, reaction (1), and exothermic partial oxidation, reaction (2). This is usually referred to as autothermal reforming.

Some processes for synthesis gas generation have been used commercially for decades. Hence the amount of literature dealing with the subject is large. More details can be found in paper II, paper III or in the review papers by Rostrup-Nielsen [16] and Dybkjær [17].

2.2 H_2 production from synthesis gas

Synthesis gas can be used for production of H_2. CO and H_2O are converted to CO_2 and H_2 through water-gas shift, reaction (4).

Water-gas shift: $CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H_{700} = -38$ kJ/mol (4)

Water-gas shift takes place in a separate reactor vessel, typically operating at temperatures in the order of 300-500 ºC. Additional steam can be added if improved CO conversion is wanted. This is usually not needed for synthesis gas produced by steam reforming. If very low CO concentration is required, the first shift reactor is followed by a second reactor operating at lower temperature.

After the water-gas shift, a gas mixture consisting mainly of H_2 and CO_2 is obtained. In a steam reforming process there may by substantial amounts of unreformed CH_4 present as well. H_2 is separated from impurities in one or more purification steps.

The primary alternative for H_2 purification is pressure swing adsorption. Impurities are adsorbed in a bed of solid adsorbent at elevated pressure while H_2, which is highly volatile and has low polarity, passes straight through the bed. When the bed is full it is disconnected from the process and the pressure is decreased, whereby most of the impurities are released. The impurities are called pressure swing adsorption offgas and consists of CO_2, small amounts of CO, unreformed CH_4, and some H_2 that is needed for purging and regeneration of the bed. The offgas has substantial heating value and can be used as fuel, for example in a steam reformer furnace. By using multiple adsorbers and a mixing drum it is possible to provide constant gas flows. H_2 recovery is limited to about 90%. The product purity is very high, 99.99% or higher. More information about pressure swing adsorption can be found in paper II, or in the report by Stöcker et al [18] which is available via UOP, a process design company that has long experience of pressure swing adsorption.

Another option for H_2 purification is absorption. The shifted synthesis gas is scrubbed with a solvent that interacts physically or chemically with impurities but not

with H_2. Amine solvents such as MEA, DEA and MDEA are well-suited for separation of H_2 and CO_2. The resulting CO_2 rich solvent is pumped to a separate stripper column where the solvent is regenerated and CO_2 is released. Solvent regeneration consumes considerable amounts of energy and typically takes place at a temperature of 100-140 ºC and low pressure. Additional purification steps are needed if high purity H_2 is required. More details can be found in the IPCC special report on carbon dioxide capture and storage [8] or in the paper by Veawab et al [19].

2.3 H_2 from natural gas with CO_2 capture

As mentioned in section 1.3 above, about 7 million ton CO_2/year is captured during synthesis gas generation [8]. Much of this CO_2 is captured in old plants that utilize absorption for separation of H_2 and CO_2. For such facilities the energy penalty for CO_2 capture is small since almost pure CO_2 is obtained when the absorbing solvent is regenerated. For steam reforming the capture efficiency is limited though, since only CO_2 present in the process gas is captured and additional fuel is needed for the endothermic reforming reactions. Modern facilities for production of high purity H_2 utilize steam reforming and pressure swing adsorption. Here no CO_2 is provided in separate process streams so additional gas separation would be needed for CO_2 capture. Process studies describing H_2 production by reforming of natural gas with CO_2 capture by amine absorption have been presented by Consonni et al [20], Audus et al [21] and Kaarstad et al [22].

Reforming of natural gas with CO_2 capture could also be used for power generation with pre-combustion CO_2 capture. In this case, the H_2 produced should be used as fuel in a combined cycle power plant closely integrated with the reformer plant. In later years such processes has been examined quite extensively. Corradetti et al [23] have examined autothermal reforming with CO_2 capture by absorption with MDEA solvent. Ertesvåg et al [24] and Undrum et al [25] have examined autothermal reforming with CO_2 capture by chemical absorption. Lozza and Chiesa [26, 27] have examined steam reforming with CO_2 capture by absorption with DEA solvent, and partial oxidation and

autothermal reforming with CO_2 capture either by absorption with DEA solvent or physical absorption.

2.4 Chemical-looping combustion

Chemical-looping combustion is a novel process for heat and power generation with inherent CO_2 capture. It has also been called unmixed combustion since direct contact between fuel and combustion air is avoided. Instead, a solid oxygen carrier performs the task of bringing oxygen from the air to the fuel. Thus, the produced CO_2 is not diluted with N_2 and can easily be sequestrated. Suitable oxygen carriers are particles of metal oxide such as Fe_2O_3, NiO, CuO or Mn_3O_4. In this thesis, the abbreviation Me is used to describe a generic oxygen carrier in its reduced form while MeO is used for its oxidized form.

The general ideas behind chemical-looping combustion was introduced in 1983 by Richter and Knoche [28], who suggested a fuel oxidation reaction scheme involving two intermediate reactions with a metal oxide as oxygen carrier. A basic chemical-looping combustion system, shown in figure 6, has two reactor vessels, one for air and one for fuel.

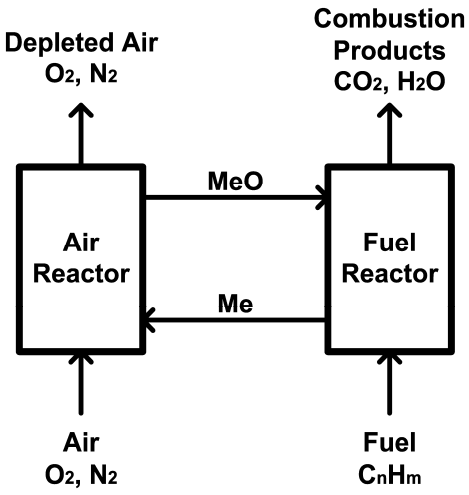


Figure 6. The principles of chemical-looping combustion.

The oxygen carrier circulates between the reactors. In the air reactor, it is oxidized with O_2 from the combustion air according to reaction (5). In the fuel reactor, it is

reduced to its initial state by the fuel, which in turn is oxidized to CO_2 and H_2O according to reaction (6).

Air reactor: $O_2 + 2Me \rightarrow 2MeO$ (5)

Fuel reactor: $C_nH_m + (2n+½m)MeO \rightarrow nCO_2 + (½m)H_2O + (2n+½m)Me$ (6)

The amount of energy released or required in the reactor vessels depends on the nature of the oxygen carrier and the fuel, as well as on the temperature of reaction. Reaction (5) is strongly exothermic. With hydrocarbon fuels, reaction (6) is endothermic if NiO, Fe_2O_3 or Mn_3O_4 is used as oxygen carrier, but exothermic if CuO is used. With H_2 or CO as fuel reaction (6) is slightly exothermic for all mentioned oxygen carriers. If reaction (6) is endothermic the oxygen-carrier particles must be able to transport heat from the strongly exothermic air reactor to the fuel reactor, in addition to transporting oxygen to the fuel.

The net energy released in the reactor system is the same as for ordinary combustion. This is apparent since combining reaction (5) and reaction (6) yields reaction (7), which is complete combustion of the fuel with O_2.

Total reaction: $C_nH_m + (n+¼m)O_2 \rightarrow (n)CO_2 + (½m)H_2O$ (7)

Chemical-looping combustion has many potential benefits compared to conventional combustion. The exhaust from the oxidation reactor is harmless and consists mainly of N_2. There should be no thermal formation of NO_X since regeneration of the oxygen carrier takes place without flame and at moderate temperature. The gas from the reduction reactor consists of CO_2 and H_2O so a condenser is the only equipment needed to obtain pure CO_2 for sequestration.

In later years, when the interest for carbon sequestration has increased, chemical-looping combustion has become an active research issue. The research has focused on experimental and theoretical investigations of possible oxygen-carriers and on process studies regarding how chemical-looping combustion could be used for power generation. An overview of the research dealing with oxygen-carriers for chemical-

looping combustion can be found in the works of Cho [29], Johansson [30] and Adánez et al [31]. An overview of various subjects regarding chemical-looping combustion, such as design of experimental reactors, power production with CO_2 capture and more about oxygen-carriers can be found in the doctoral theses by Brandvoll [32], Johansson [33] and Wolf [34].

In practice, a chemical-looping combustion process could be designed in several ways, but circulating fluidized beds are likely to have an advantage over other alternatives since this design provides good contact between gas and solids and allows a smooth flow of oxygen carrier between the reactors. Continuous chemical-looping combustion in circulating fluidized beds has been demonstrated by Lyngfelt et al [35], Ryu et al [36], Johansson [33], Abad et al [37] and Adanez et al [38]. More detailed descriptions of chemical-looping combustion can be found in paper II and paper III.

2.5 Chemical-looping reforming

Chemical-looping reforming utilizes the same basic principles as chemical-looping combustion, see figure 7.

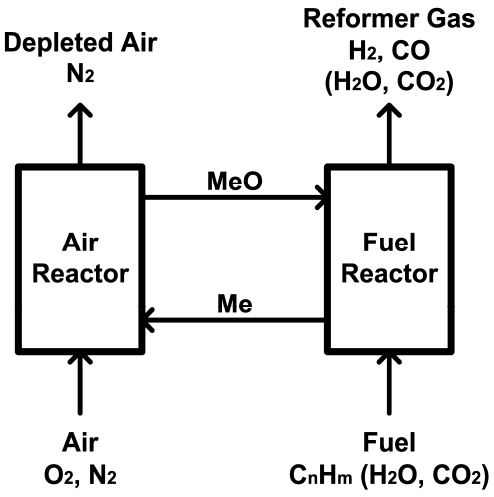


Figure 7. The principles of chemical-looping reforming.

The difference compared to chemical-loping combustion is that the wanted products are not heat but H_2 and CO. Therefore the air to fuel ratio is kept low to prevent the

fuel from becoming completely oxidized to CO_2 and H_2O. Chemical-looping reforming could be described as a process for partial oxidation of hydrocarbon fuels where chemical-looping is used as a source of undiluted oxygen. H_2O or CO_2 can be added to the fuel if steam reforming or CO_2 reforming is wanted.

Chemical-looping reforming, as described in figure 7, was proposed in 2001 by Mattisson et al [39]. Oxygen carriers specifically for chemical-looping reforming have been experimentally examined by Zafar et al [40], who performed tests in a fluidized-bed reactor with oxygen-carrier particles as fluidizing agent, and by Mattisson et al [41]. These two studies indicates high reaction rate and good selectivity towards H_2 and CO for oxygen carriers with NiO as active phase, while oxygen carriers based on Fe_2O_3, CuO and Mn_3O_4 suffered from poor selectivity and produced CO_2, H_2O and unreformed CH_4 rather than CO and H_2. Chemical-looping reforming has also been examined in a process study by Johansson [42].

A few process concepts comparable to chemical-looping reforming have also been proposed. Stobbe et al [43] have suggested a process involving oxidation and reduction of manganese oxide. Fathi et al [44], Gavalas et al [45] and Jalibert et al [46] has suggested and examined partial oxidation of CH_4 by oxidation and reduction of CeO_2 promoted with noble-metal catalysts, while Shen et al [47, 48], Zeng et al [49], Li et al [50] and Bjørgum [51] has studied the possibility to use mixed-oxide perovskites such as $La_{(1-x)}Sr_xFe_{(1-y)}Co_yO_{3-\delta}$ for the same purpose.

In the experiments and models described in this thesis, NiO has been used as oxygen carrier and CH_4 or CH_4 rich natural gas has been used as fuel. With a reactor temperature of 1200 K, reaction (8) occurs in the air reactor:

Ni regeneration: $Ni + ½O_2 \rightarrow NiO$ $\Delta H_{1200} = -235$ kJ/mol (8)

In the fuel reactor reaction (9-12) may occur, depending on the air factor. Steam or CO_2 could be added to the fuel to enhance the relative importance of reaction (11) or reaction (12) respectively.

Oxidation:	$CH_4 + 4NiO \rightarrow CO_2 + 2H_2O + 4Ni$	$\Delta H_{1200} = 136$ kJ/mol	(9)
Partial oxidation:	$CH_4 + NiO \rightarrow CO + 2H_2 + Ni$	$\Delta H_{1200} = 211$ kJ/mol	(10)
Steam reforming:	$CH_4 + H_2O \rightarrow CO + 3H_2$	$\Delta H_{1200} = 226$ kJ/mol	(11)
CO_2 reforming:	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	$\Delta H_{1200} = 259$ kJ/mol	(12)

The overall reaction enthalpy for the reactor system varies as the relative importance between reactions (9-12) is altered. It shall be noticed that reaction (11-12) are strongly endothermic and do not provide any Ni to be reoxidized with the exothermic reaction (8). Consequently, steam reforming and CO_2 reforming should not be allowed to dominate since that would make the reactor system endothermic. External heating of the fuel reactor at relevant temperatures would be highly unfavourable from a technical point of view.

The reformed gas is a mixture consisting of H_2, H_2O, CO and CO_2, and could be used as feedstock for chemical processes or for production of H_2, just as synthesis gas from other reforming processes. It is possible that there will be some unreformed CH_4 in the reformer gas if the reactor temperature is not sufficiently high. If thermodynamic equilibrium is assumed, a fuel reactor temperature in the order of 800 °C should be sufficient to achieve 99% conversion of CH_4 at atmospheric pressure. At elevated pressure, temperatures over 1000 °C might be needed. Chemical-looping reforming is described in greater detail in paper III.

3. METHODOLOGY AND RESULTS

3.1 Summary of paper I

Paper I includes a process study showing how chemical-looping reforming could be used to produce H_2 with CO_2 capture. A thermodynamic analysis was conducted to investigate the basic characteristics, potential efficiency, and key parameters of 6 relevant process configurations. The result was compared to a reference process, which was H_2 production by steam reforming with CO_2 capture by amine absorption.

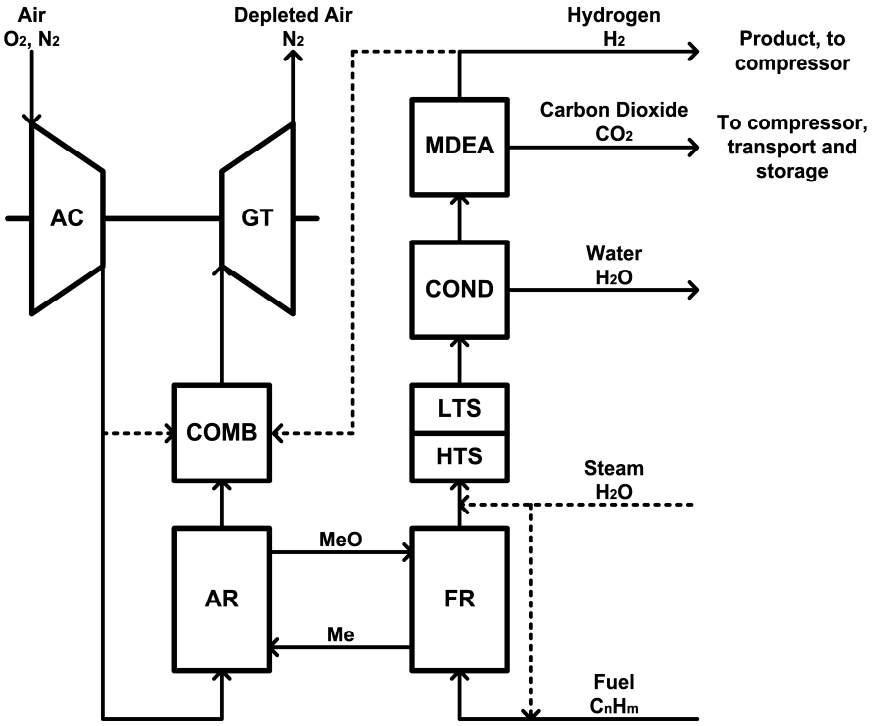


Figure 8. Schematic description of cogeneration of H_2 and power by chemical-looping reforming at elevated pressure, as proposed in paper I. Heat exchangers and possible integration with external steam cycle are not shown.

A schematic description of the process layout for reforming at elevated pressure proposed in paper I is shown in figure 8. If desired, the fuel is mixed with steam before the fuel reactor (FR). Air is compressed (AC) before entering the air reactor (AR). The outlet from the reformer reactor is cooled and additional steam is added prior to the

high-temperature shift (HTS) and low-temperature shift (LTS). H_2O is removed from the shifted gas in a condenser (COND) before CO_2 is captured by absorption with MDEA solvent (MDEA). CO_2 for sequestration is obtained by regenerating the MDEA solvent in a stripper column. If wanted, some of the produced H_2 could be burned in a separate combustor (COMB) to increase the power output of the gas turbine (GT). Excess heat could be used for power generation in a separate steam cycle. Similar process layout was assumed for atmospheric processes, but for these there was no need for air compression or gas turbine.

The fuel reactor temperature was about 880 ºC for atmospheric systems and 1000-1170 ºC for pressurized systems, which was assumed to be operating at 15 bar. Captured CO_2 was compressed to 100 bar. Produced H_2 was compressed to 20 bar.

It was concluded that chemical-looping reforming at atmospheric pressure easily could have large H_2 yield, but the power required to compress produced H_2 to suitable product pressure was considerable. For the pressurized processes, integration with a gas turbine for cogeneration of H_2 and power seemed logical; otherwise the energy penalty for air compression would become large. When H_2 compression was considered the pressurized processes showed better overall efficiency than the atmospheric processes. Weighted reformer efficiency in the order of 80% or higher seemed obtainable, with net power demand taken in consideration.

3.1.1 Comments on paper I

In paper I, it was assumed that an aqueous solution of MDEA was used for CO_2 capture in all examined processes. MDEA is often used for CO_2 capture in synthesis gas processes and is attractive compared to MEA due to the low energy demand for regeneration. But while it would be technically possible to capture CO_2 with MDEA in all cases proposed in paper I, it may not be the best choice for the atmospheric chemical-looping reforming processes or for CO_2 capture from the flue gases from a steam reforming furnace. These alternatives provide CO_2 at relatively low partial pressure and with MDEA as absorbing solvent this would result in large equipment

size. A stronger absorbing solvent such as MEA or addition of a synthesis gas compressor would likely be necessary.

As mentioned above, calculations were also made for a reference process consisting of steam reforming with CO_2 capture. For this process, the temperature difference between the furnace and the reformer tubes was set to a rather low value. This could be realized by so called heat-exchange reforming. At present however, it is questionable whether this kind of technology is commercially attractive [16, 17, 52].

An updated comparative process study is presented in this thesis. Here a few alternative processes such as steam reforming with CO_2 capture by chemical-looping combustion have also been included. The same models have been used as in paper I and paper II, with some minor modifications. See section 3.4 below for details.

3.2 Summary of paper II

In a conventional steam reforming plant, the energy needed for the highly endothermic steam reforming, reaction (1), is provided by combustion of pressure swing adsorption offgas and extra fuel in a furnace. The reformer tubes are located inside the furnace and heat transfer is due to radiation. In paper II, it is proposed that the furnace could be replaced by chemical-looping combustion and that the reformer tubes could be located inside the fuel reactor, or possibly in a separate fluidized bed heat exchanger. A schematic description of the reactor system proposed in paper II is found in figure 9 below.

The suggested process layout would provide at least three advantages compared to conventional steam reforming. Firstly, it would provide inherent CO_2 capture with no energy penalty compared to conventional steam reforming. Secondly, it would eliminate the problem with formation of thermal NO_X in the reformer furnace since chemical-looping combustion operates without flame and at moderate temperature. Thirdly, it would make it possible to reduce the flue gas temperature compared to conventional steam reforming without increasing the length of the reformer tubes. This would be possible since fluidized-bed heat transfer results in high convective heat transfer coefficient on the outside of the reformer tubes. This may be a significant

advantage. In a conventional steam reforming furnace, the heat transfer from the flue gas to the reformer tube surface is mostly due to radiation. Very high furnace temperature is needed and typically more heat is bound in the flue gases than what can be utilized within the process for preheating of fuel and steam. This spare heat is typically used for production of export steam, which is a much less desirable product than H_2. Reduced flue gas temperature would mean that H_2 production could be increased at the expense of reduced steam export.

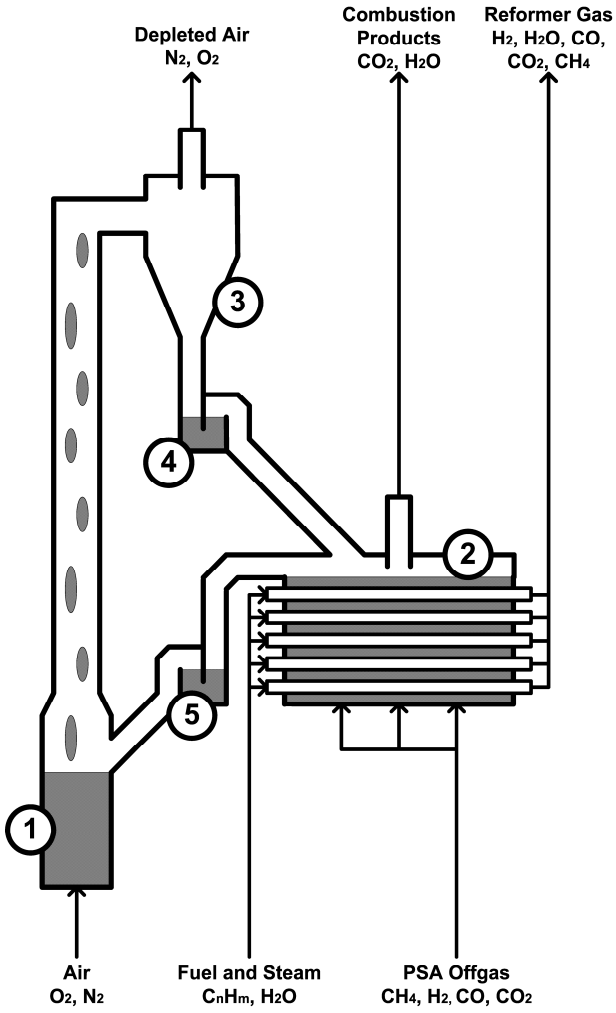


Figure 9. Reactor system for steam reforming of natural gas with CO_2 capture by chemical-looping combustion. (1) is the air reactor, (2) is the fuel reactor which also contains the reformer tubes, (3) is a cyclone for particle separation, (4) and (5) are particle-gas locks that prevents leakage between the reactors. The particle-gas locks are fluidized with small amounts of steam.

In order to examine the potential efficiency of the proposed reactor system, a model that describes H_2 production with CO_2 capture by chemical-looping combustion and H_2 purification by pressure swing adsorption was made. The model calculated key operative parameters such as temperatures, gas compositions, gas flows and necessary heating and cooling throughout the process. The outlet of the reformer tubes was set to 24 bar. The outlet temperature of the reformer tubes was varied from 750-850 ºC. The steam to fuel ratio in the feedstock was adapted to suit the temperature of reforming. A schematic description of the process can be found in figure 10.

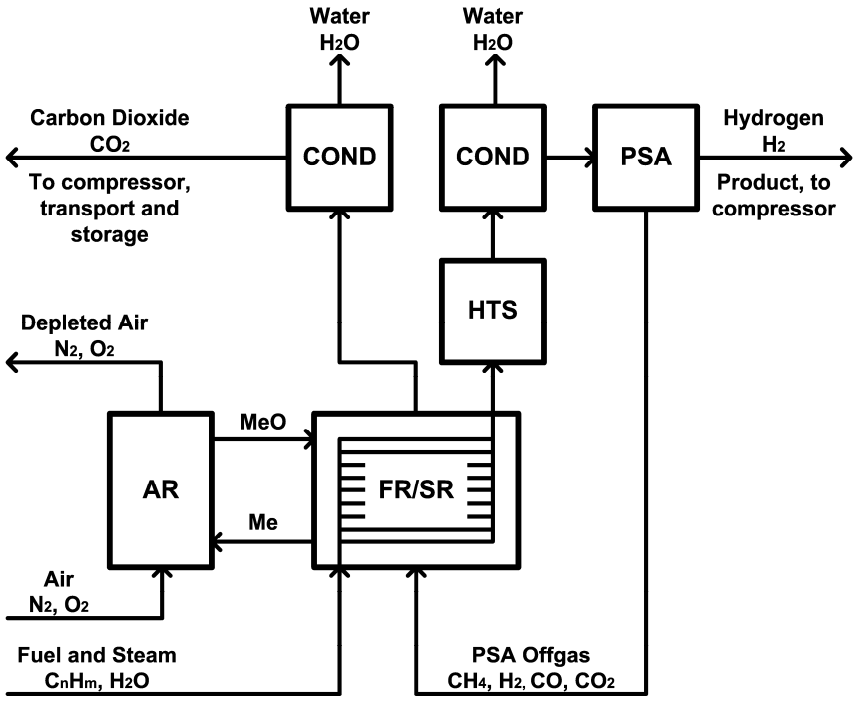


Figure 10. Schematic description of the H_2 plant proposed in paper II. Heat exchangers, fans and compressors are not shown.

The air reactor (AR) and fuel reactor (FR) is operating at atmospheric pressure. Steam reforming (SR) takes place at elevated pressure in reformer tubes packed with catalyst that is located inside the fuel reactor. The reformer gas is treated in a single water-gas shift reactor (HTS). Water is removed from the process stream by cooling in a condenser (COND) before it enters a pressure swing adsorption unit (PSA). Produced H_2 is delivered at elevated pressure, but a fraction is needed for purging and

regenerating the adsorbers. The resulting pressure swing adsorption offgas consist of CO_2, purge H_2, unconverted CH_4 and small amounts of CO. The offgas is delivered at low pressure and is used as fuel and fluidizing gas in the fuel reactor. Pure CO_2 for sequestration is obtained by chemical-looping combustion.

It was found that process layout described in figure 10 would make it possible to reduce steam export to a minimum and eliminate the need for other fuel than pressure swing adsorption offgas to provide energy for the endothermic reforming reactions. This is due to the reduced flue gas temperature. The reformer efficiency was 76.7-84.6%, excluding power for CO_2 compression. Increasing the temperature of reforming increased the reformer efficiency. Higher temperature improved conversion of CH_4 to reagents, so less H_2O needed to be produced and added to the CH_4 to obtain desired product composition.

In addition to the process study, a second model describing the properties of one single reformer tube surrounded by a hot fluidized bed was made. The two models was combined and used to make a tentative design of a reactor system and a heat-exchanger network for a plant with a H_2 production of 1000 mol/s, which corresponds to a fuel flow of roughly 300 MW. It was found that the reactor dimensions, particle flows, gas flows, pressure drops and temperature levels seemed reasonable. Produced offgas would be sufficient for fluidization of the fuel reactor. Setting up a suitable heat exchanger network was straightforward. The required amount of oxygen-carrier particles was quite high, 345 kg for each mol/s processed CH_4 for the base case. This should be more than enough to obtain complete conversion of the fuel with many types of oxygen carriers. The amount could be reduced by decreasing the distance between the reformer tubes in the fuel reactor, or changing the geometry of the fuel reactor.

3.2.1 Comments on paper II

In order to make a comparison with chemical-looping reforming, steam reforming with CO_2 capture by chemical-looping combustion has been included in the comparative process study presented in section 3.4 of this thesis.

3.3 Summary of paper III

Paper III describes continuous chemical-looping reforming of natural gas in a laboratory reactor consisting of two interconnected fluidized beds. In order to make it possible to reach suitable operating temperatures the whole reactor system was enclosed in an electrically heated furnace. 350 g of particles consisting of 60 wt% NiO and 40 wt% $MgAl_2O_4$ were used as bed material, oxygen carrier and reformer catalyst. The particles were prepared by freeze granulation and sintered at 1300 °C for 6 hours before they were sieved to a size of 90-212 μm. There was a continuous circulation of particles between the reactors. Natural gas was used as fuel. In the fuel reactor, the particles were reduced by the fuel, which in turn was partially oxidized to H_2, CO, CO_2 and H_2O. In the air reactor the reduced oxygen carrier was reoxidized with air.

The rector is shown in figure 11. A detailed description can be found in paper III or in the work of Johansson [33].

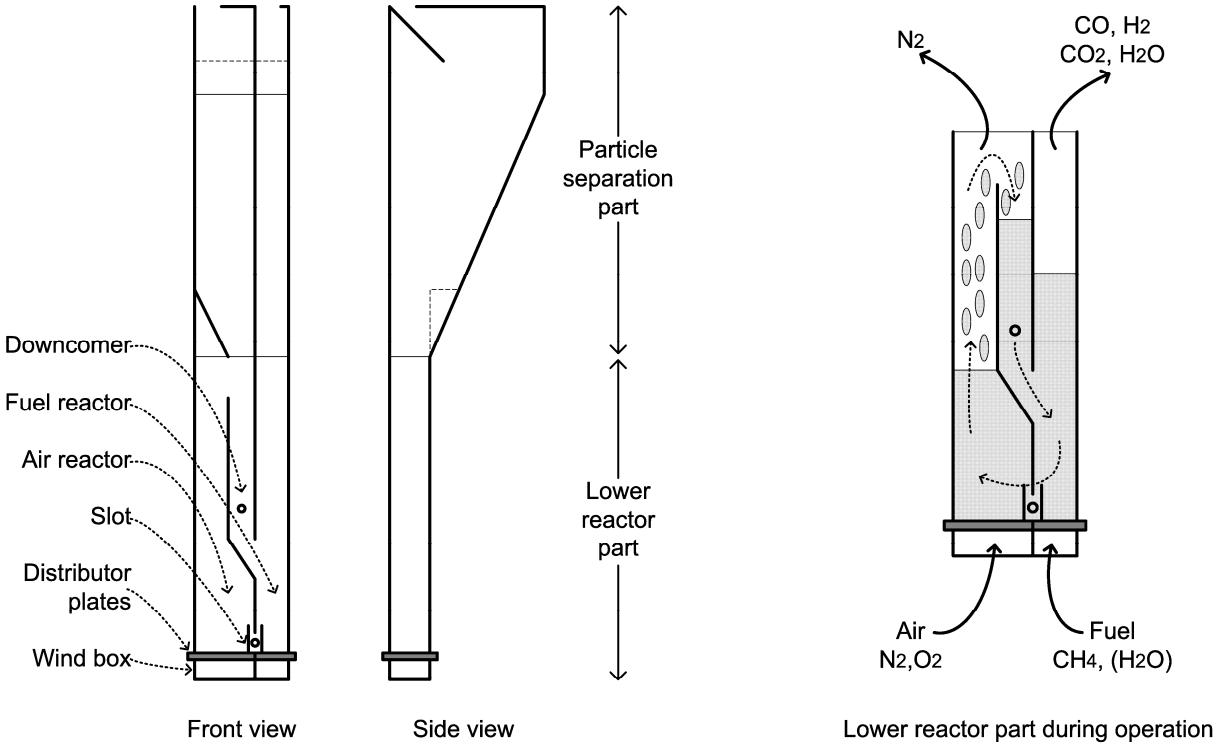


Figure 11. The laboratory reactor used in paper III.

In total, 24 hours of reforming with dry natural gas and 17 hours with 75 vol% natural gas and 25 vol% steam were performed. The addition of this amount of steam is in the same order of magnitude as was proposed in paper I and seems reasonable if an autothermal process is desired. Complete conversion of natural gas was achieved and the selectivity towards H_2 and CO was good. The fuel reactor temperature was 820-930 ºC. All measurements were made on dry gas, after cooling and condensation.

Formation of solid carbon was identified as a potential problem and was apparent for some of the experiments with dry natural gas since small amounts of carbon were accumulating in the fuel reactor. If it was assumed that the gas from the fuel reactor was at thermodynamic equilibrium the level of carbon formation could be estimated with a species balance. With 25 vol% steam added to the fuel there was no or very small accumulation of carbon in the reactors and the estimated carbon formation was small. These two factors indicate that the carbon formation was indeed low when extra steam was added to the CH_4.

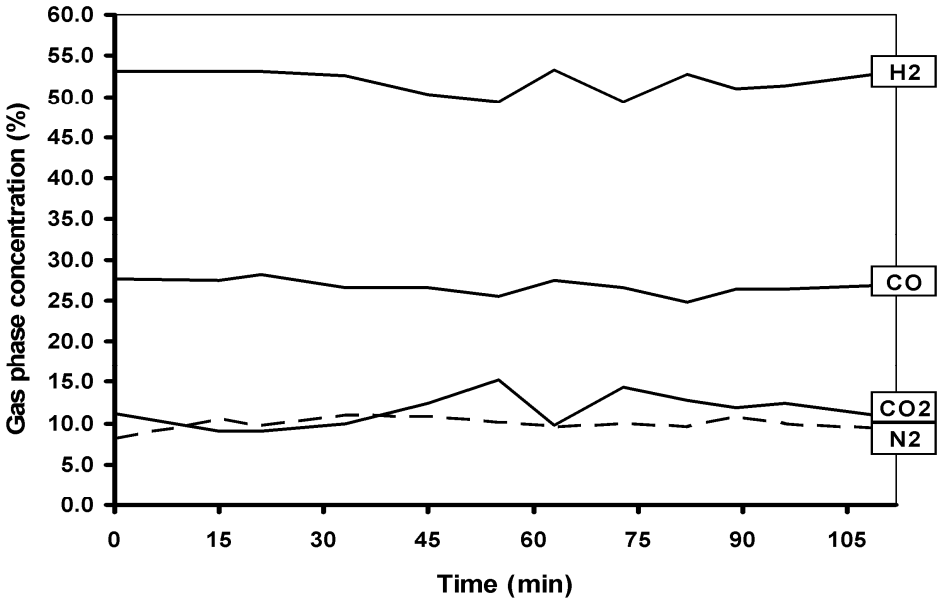


Figure 12. Example of dry gas composition after the fuel reactor for chemical-looping reforming of natural gas with 25 vol% steam at roughly 900 ºC.

For most of the experiments the amount of oxygen that reacted with the fuel compared to what was needed for combustion was 0.40-0.50, which corresponds to a

dry gas composition of ≈55% H_2, ≈25% CO, ≈10% CO_2 and ≈10% N_2. An example of the gas composition for a typical experiment with chemical-looping reforming of natural gas with 25 vol% steam is shown in figure 12 above.

In figure 12, it can be seen that the reformed gas was diluted by N_2. This was due to gas leakage between the two reactor halves, likely through the slot and maybe also through the downcomer. Typically 1-3% of the N_2 added with air in the air reactor leaked to the fuel reactor and 20-40% of the carbon added to the fuel reactor ended up in the air reactor. The gas leakage from the fuel reactor to the air reactor was quite high. This was expected, since the pressure was about 200 Pa higher in the fuel reactor. The pressure in the fuel reactor was controlled by altering the height of a water column in a water seal, located after the reactor.

33-44% of the available NiO on the oxygen-carrier particles was reduced to Ni during operation. At this point steady state was achieved and the remaining NiO was not reduced. The oxygen-carrier particles did not agglomerate, but lumps were found in the air reactor at the end of the test series. A likely explanation for this phenomenon is the low gas velocity used, 0.1-0.5 m/s. The lumps were soft and it seems highly unlikely that they would have formed in a real-world riser where the gas velocity should have been in the order of 5 m/s.

The experiments presented in paper III confirm that continuous chemical-looping reforming in circulating fluidized beds is feasible and should be further investigated.

3.4 Comparative process study of H_2 production with CO_2 capture

In order to make a comparison between chemical-looping reforming and steam reforming with CO_2 capture by chemical-looping combustion, an updated process study examining the concepts has been made. Two steam reforming processes with CO_2 capture by amine absorption have been included as reference. The same models were used as in paper I and paper II, with some modifications. The following process alternatives have been included:

1. Chemical-looping reforming at atmospheric pressure with CO_2 capture by absorption with MEA solvent (CLR).
2. Chemical-looping reforming at atmospheric pressure integrated with a steam cycle with compression of synthesis gas prior to CO_2 capture by absorption with MDEA solvent (CLR/SC).
3. Pressurized chemical-looping reforming integrated with a gas turbine with CO_2 capture by absorption with MDEA solvent (CLR/GT).
4. Steam reforming with CO_2 capture by chemical-looping combustion (SR/CLC).
5. Steam reforming with CO_2 capture by MDEA scrubbing following the water-gas shift and condenser (SR/MDEA).
6. Steam reforming with CO_2 capture by MEA scrubbing of flue gas after the reformer furnace (SR/MEA).

A description of each concept can be found in section 3.4.1-3.4.6 below. The processes have been considered as stand-alone plants optimized for H_2 production. Conservative process parameters have been used. It would be possible to increase preheating and reactor temperature slightly, which could be beneficial in some cases. The aim with the study has been to make a general comparison between the concepts. The following assumptions have been used:

- The fuel is CH_4 which is delivered to the plant at a suitable pressure and a temperature of 20 ºC.
- For chemical-looping reforming, the fuel is mixed with one third steam, which is assumed to prevent carbon formation in the fuel reactor.
- The product is H_2 at a pressure of 20 bar. If amine absorption is used for CO_2 capture the produced H_2 will also contain impurities such as CH_4, CO and CO_2 so further purification would be needed for some applications. This has not been considered.
- The gas from the reforming reactors and the water-gas shift reactors are assumed to be at thermodynamic equilibrium.

- Complete conversion to CO_2 and H_2O is assumed for chemical-looping combustion.
- No heat losses have been considered, so real-world H_2 plants would have slightly different process parameters and slightly lower efficiency. Steam reforming plants generally have very high thermal efficiency, 95% or higher [16].
- Preheating of fuel, steam and air proceeds to the same temperature.
- The power demand for pumps for feed-water and amine solvent, which is very small compared to the power consumption for gas compression, has been neglected.
- Amine absorption captures 95% of the CO_2 available in the process stream. Regeneration of the amine solvent takes place in a stripper column at 130 ºC and atmospheric pressure. Heat demand for the regeneration is set to 140 kJ/mol CO_2 for MEA and to 60 kJ/mol CO_2 for MDEA. Reported heat demand for amine regeneration varies much between different sources, and these numbers have been selected after consulting the work of Veawab et al [19] and IPCC:s special report on carbon dioxide capture and storage [8].
- Pressure swing adsorption produces pure H_2 and the recovery rate is limited to 90%. The offgas is released at about atmospheric pressure.
- 10% excess air is used for combustion and chemical-looping combustion.
- CO_2 for sequestration is compressed to 100 bar. Transport and storage of CO_2 has not been considered.
- Multi-stage compression with intercooling is considered. CO_2 compression takes place in three steps while air, H_2 and synthesis gas is compressed in two steps.
- For chemical-looping systems, the oxygen-carrier particles consist of 50 mass% NiO and 50 mass% Al_2O_3. The mass flow of oxygen carrier is set to a value so that the temperature difference between the fuel reactor and air reactor is 50 K.
- The isentropic efficiency of fans, pumps, compressors and turbines have been set to 85%, while the mechanical efficiency have been set to 99%.

- Ambient temperature is 20 ºC and ambient pressure is 1 bar.
- The minimum temperature difference for heat exchange is 20 K.
- The pressure drop has been set to 1.0 bar for reformer tubes, 0.5 bar for water-gas shift, absorption and pressure swing adsorption and 0.1 bar for fluidized-bed reactors.

Process data for the basic cases in the comparative study is summarized in table 1. An explanation of abbreviations and subscripts can be found in the appendix.

	CLR	**CLR/SC**	**CLR/GT**	**SR/CLC**	**SR/MDEA**	**SR/MEA**
$T_{air\ reactor}$ (°C)	880	950	1050	960	-	-
$T_{fuel\ reactor}$ (°C)	830	900	1000	910	-	-
$T_{reformer,\ out}$ (°C)	-	-	-	810	850	810
$T_{reformer\ furnace}$ (°C)	-	-	-	-	1100	1100
CH_4 conversion (%)	99.8	99.9	99.0	79.0	93.4	79.0
$T_{preheating}$ (°C)	130	500	600	600	600	540
(H_2O/CH_4) in fuel mix	0.50	0.50	0.50	3.50	5.00	3.50
(O_2/CH_4) for CLR	0.71	0.60	0.60	-	-	-
$p_{reforming}$ (bar)	1.0	1.0	10.0	21.0	21.5	21.0
(H_2O/CO) in HTS	2.0	2.3	2.5	-	-	-
T_{HTS} (°C)	310	310	380	400	310	400
T_{LTS} (°C)	200	200	230	-	250	-
H_2 recovery in PSA (%)	-	-	-	90.0	68.2	81.0
$p_{CO2,\ ABS}$ (bar)	0.41	5.35	2.47	-	4.00	0.36
$H_{REG,\ ABS}$ / $Hi_{CH4,\ in}$ (%)	-16.32	-7.02	-6.93	-	-6.56	-16.58
$E_{COMP,\ ABS}$ / $Hi_{CH4,\ in}$ (%)	-1.80	-	-	-	-	-0.71
$E_{(GT/SC)}$ / $Hi_{CH4,\ in}$ (%)	-	+2.95	+4.60	-	-	-
$E_{COMP,\ air}$ / $Hi_{CH4,\ in}$ (%)	-0.12	-0.10	-2.87	-0.11	-	-
$E_{COMP,\ syngas}$ / $Hi_{CH4,\ in}$ (%)	-	-7.14	-	-	-	-
$E_{COMP,\ H2}$ / $Hi_{CH4,\ in}$ (%)	-3.55	-	-0.87	-	-	-
$E_{COMP,\ CO2}$ / $Hi_{CH4,\ in}$ (%)	-1.80	-1.81	-1.78	-1.93	-1.69	-1.83
E_{net} / $Hi_{CH4,\ in}$ (%)	-7.27	-6.10	-0.93	-2.04	-1.69	-2.54
$n_{H2,\ out}$ / $n_{CH4,\ in}$	2.56	2.79	2.74	2.77	2.53	2.49
$Hi_{H2,\ out}$ / $Hi_{CH4,\ in}$ (%)	77.9	84.1	82.7	83.4	76.2	75.0
Produced H_2 purity (%)	97.5	97.9	97.4	≈100	≈100	≈100
CO_2 capture (%)	93.5	93.9	92.6	≈100	87.6	95
η_{ref} (%)	64.7	73.5	81.1	79.8	73.3	70.7

Table 1. Process data for the base cases in the comparative process study.

The weighted reformer efficiency, η_{ref} in table 1, has been calculated with expression (13).

$$\eta_{ref} = \{ [(n_{H2,\,out}/n_{CH4,\,in}) + E_{net} /(Hi_{H2} \times \eta_{el})] \times Hi_{H2} \} / Hi_{CH4} \quad (13)$$

where

$(n_{H2,\,out}/n_{CH4,\,in})$ = Moles H_2 produced per mole CH_4 in the feedstock
E_{net} = Power surplus/demand (J/mol CH_4)
Hi_{CH4} = Lower heating value for CH_4 (802 300 J/mol)
Hi_{H2} = Lower heating value for H_2 (241 800 J/mol)
η_{el} = Reference efficiency for power generation with H_2 in combined cycle (0.58)

Process descriptions and comments can be found in section 3.4.1-3.4.7 below, where each process alternative is presented together with a schematic process scheme which shows the general principles of each process but leaves out minor operations such as fans and heat exchangers. The abbreviations used on the process schemes are explained in the appendix.

A composite curve has been included for each process alternative. A composite curve describes the sum of required heat transfer operations as a function of temperature for warm and cold process streams. A composite curve is a useful and illustrative way to represent the thermal profile of an industrial process. In a well balanced process there should be as little heat exchange as possible, as small temperature gap between the warm and cold streams as possible and as much as possible of the warm streams should be utilized for heating. For the steam reforming processes presented in section 3.4.4-3.4.6, heat transfer to the reformer tubes have not been included in the composite curve.

3.4.1 Chemical-looping reforming at atmospheric pressure

The simplest possible chemical-looping reforming system for H_2 production would be an atmospheric process without integration with any other facilities, see figure 13.

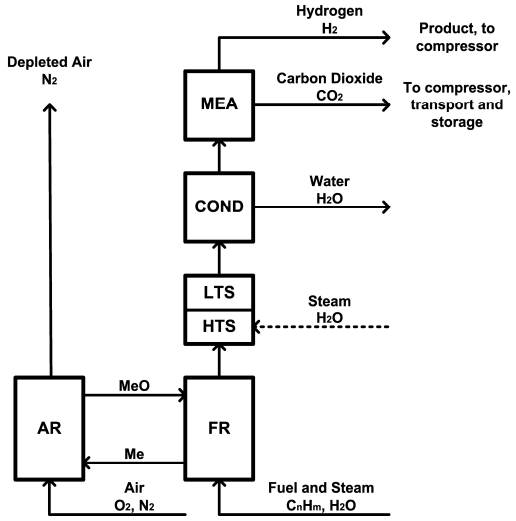


Figure 13. Schematic description of chemical-looping reforming at atmospheric pressure.

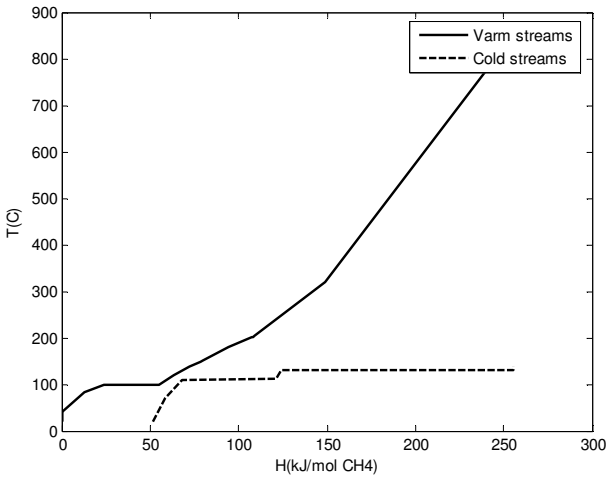


Figure 14. Composite curve for chemical-looping reforming at atmospheric pressure with no integration with other processes.

Reactor design would be straightforward. No extra features such as steam cycle or gas turbine are required. CH_4 conversion is favoured at low pressure, so there is no need for very high reactor temperatures. This may be positive with respect to oxygen carrier performance.

The CO_2 partial pressure is low after the shift reactors, so CO_2 capture will require a strong absorbing solvent such as MEA. Hence the energy penalty for regenerating the absorbing solvent is large. This can be accepted since the gas from the chemical-looping reactors contains excess heat, for which there is no other use within the process. Preheating of fuel, steam and air to high temperatures would not benefit overall efficiency. Increased preheating would only increase reactor temperature and the amount of excess heat available after the chemical-looping reactors further.

This concept has some obvious drawbacks though. Reforming involves large volumetric increase. Therefore there is a substantial energy penalty for compression of produced H_2 when reforming takes place at atmospheric pressure. The pressure after the water-gas shift is below atmospheric. Hence a separate fan is needed to overcome the pressure drop in the absorption facility. Produced H_2 will contain small amounts of CO_2, CH_4 and CO so further purification may be necessary.

In the composite curve, figure 14, it can be seen that regeneration of the amine solvent is done with heat available at high temperatures which results in exergy losses. This can be addressed if integration with other nearby processes is considered, which is done in section 3.4.2 below. The weighted reformer efficiency is about 65%, which is the lowest of the examined process concepts.

3.4.2 Chemical-looping reforming integrated with a steam cycle

This concept addresses some of the flaws with the simple atmospheric chemical-looping reforming process described above. A compressor is added after the condenser, see figure 15.

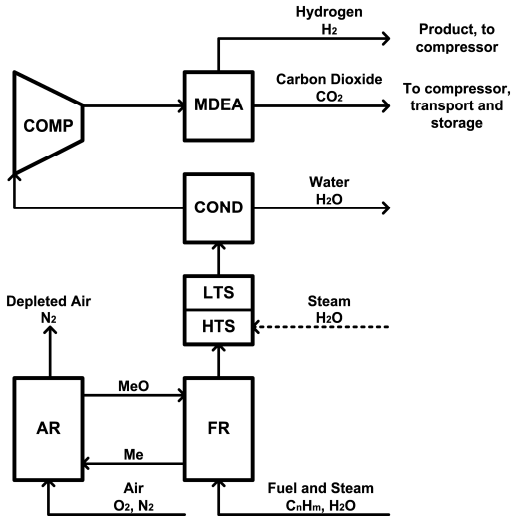


Figure 15. Schematic description of chemical-looping reforming with synthesis gas compression.

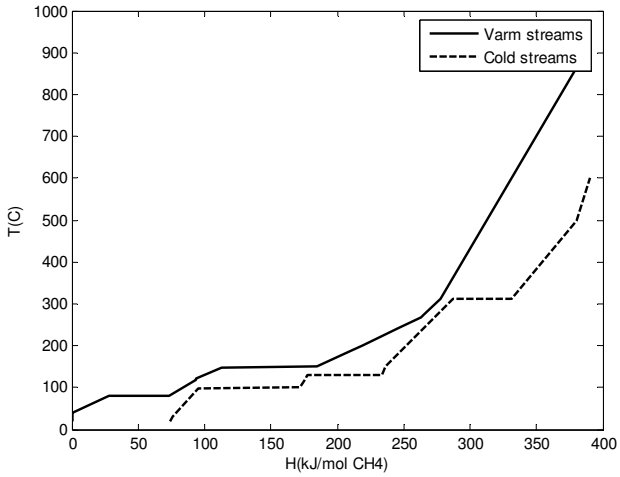


Figure 16. Composite curve for Chemical-looping reforming with synthesis gas compression and external steam cycle.

Due to the compressor, CO_2 can be captured at higher partial pressure and a less strong absorbing solvent such as MDEA can be used. This reduces the energy penalty for solvent regeneration, and integration with a steam cycle for power generation becomes a viable option.

In the example presented in table 1, integration with a single steam turbine operating with a maximum temperature of 600 ºC, a top pressure of 100 bar and a back pressure of 4.8 bar have been considered. After the turbine, the steam is cooled in a condenser which releases heat suitable for regeneration of the MDEA solvent and generation of process steam. Preheating of fuel, steam and air becomes viable and the thermal integration of the process is improved, see figure 16.

The weighted reformer efficiency is about 74%, which is a big improvement. It can be noted that this process alternative has large external power demand, despite the steam cycle. This is due to the extensive need for gas compression. CO_2 is compressed twice, since regeneration of the amine solvent is done at low pressure.

3.4.3 Pressurized chemical-looping reforming integrated with a gas turbine

Pressurized chemical-looping reforming has potential for higher efficiency than the alternatives operating at atmospheric pressure. Increasing pressure provides two obvious advantages. Firstly, the energy penalty for H_2 compression is reduced dramatically. Since there is limited use for H_2 at atmospheric pressure this is very important. Secondly, CO_2 is captured at higher partial pressure so a less strong absorbing solvent than MEA should be sufficient, even if no extra synthesis gas compressor is used. In the example found in table 1 it is assumed that CO_2 is captured with MDEA solvent. The H_2 produced will still contain impurities though, so further purification may be needed.

A pressurized process has some drawbacks as well. Integration with a gas turbine is needed or there would be a large energy penalty for the necessary air compression, see figure 17.

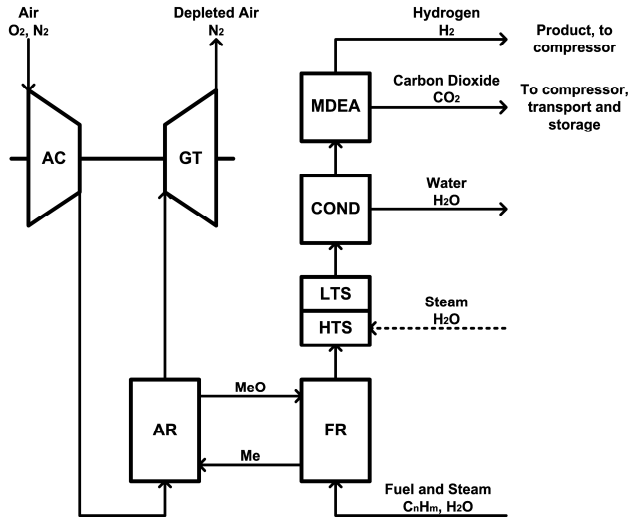


Figure 17. Schematic description of pressurized chemical-looping reforming integrated with a gas turbine.

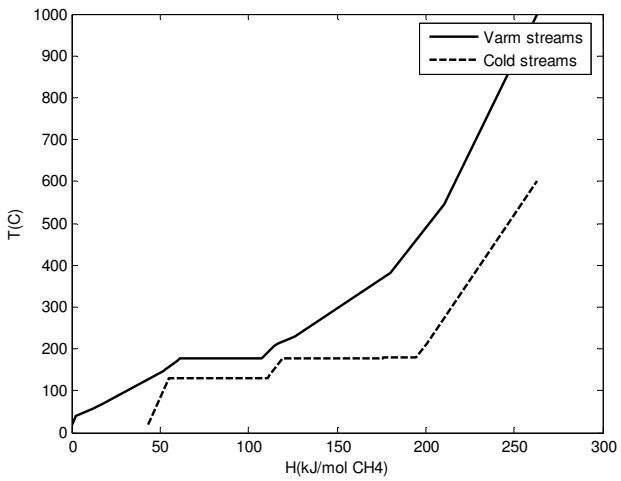


Figure 18. Composite curve for pressurized chemical-looping reforming integrated with a gas turbine.

It shall also be noticed that fuel conversion is hampered by elevated pressure, so higher reformer temperatures will be required compared to chemical-looping reforming at atmospheric pressure. Finally, it shall be pointed out that pressurized circulating fluidized beds of this type are not a well established and commercially available technology.

The weighted reformer efficiency is about 81% for the base case. Efficiency could be improved further by increasing reactor temperature, preheating and pressure, or by using an absorbing solvent that require less energy for regeneration. Adding an external steam cycle would improve the thermal integration of the process further and reduce exergy losses.

3.4.4 Steam reforming with CO_2 capture by chemical-looping combustion

Steam reforming with CO_2 capture by chemical-looping combustion, described in figure 19 below, is an interesting alternative for H_2 production with CO_2 capture. There are some obvious advantages. Integration with pressure swing adsorption for production of H_2 with very high purity would be straightforward. CO_2 is captured by

chemical-looping combustion so there should be almost 100% capture efficiency. There is no need for gas turbine, air compression or amine absorption. The reforming takes place at elevated pressure so there is no large energy penalty for H_2 compression, while the chemical-looping combustion system still can be operated at atmospheric pressure.

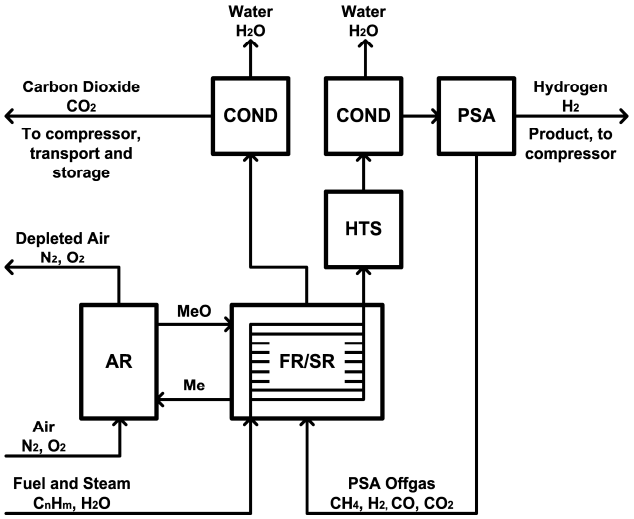


Figure 19. Schematic description of steam reforming integrated with chemical-looping combustion.

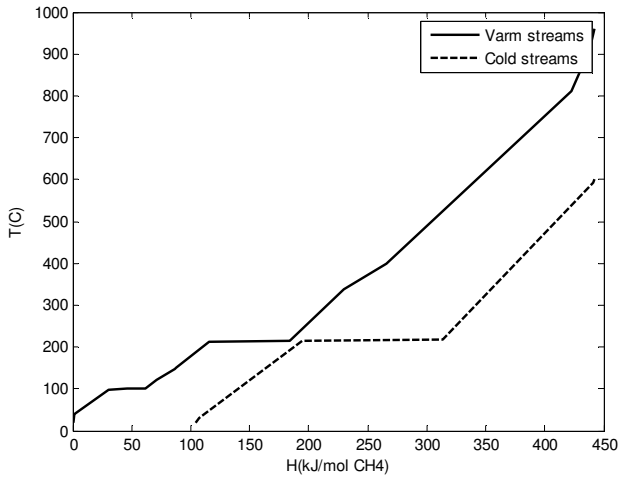


Figure 20. Composite curve for steam reforming with CO_2 capture by chemical-looping combustion.

For the example presented in table 1, the weighted reformer efficiency is about 80%. This is close to that of pressurized chemical-looping reforming. The efficiency could be improved further by increasing reformer pressure, temperature and preheating, while reducing the H_2O/CH_4 ratio. Increasing reformer temperature to 830 ºC and preheating to 650 ºC while reducing H_2O/CH_4 to 3.1 would increase efficiency about 1%.

Possible drawbacks include erosion and corrosion of the reformer tubes. It is also clear that the fuel reactor will be rather big, since it must be able to contain the reformer tubes. Hence the volume of oxygen-carrier particles that is needed will be large. Se paper II for details.

3.4.5 Steam reforming with CO_2 capture by absorption after water-gas shift

Steam reforming with CO_2 capture by absorption after the water-gas shift reactors and water removal by condensation, described in figure 21, is similar to conventional processes for H_2 production by steam reforming and has been included as reference.

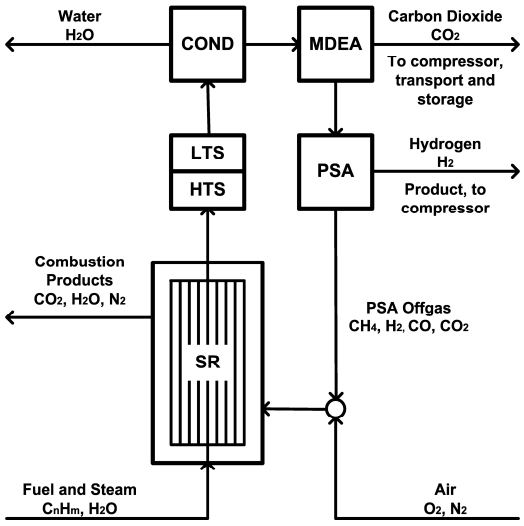


Figure 21. Steam reforming with CO_2 capture by absorption following the water-gas shift and condenser.

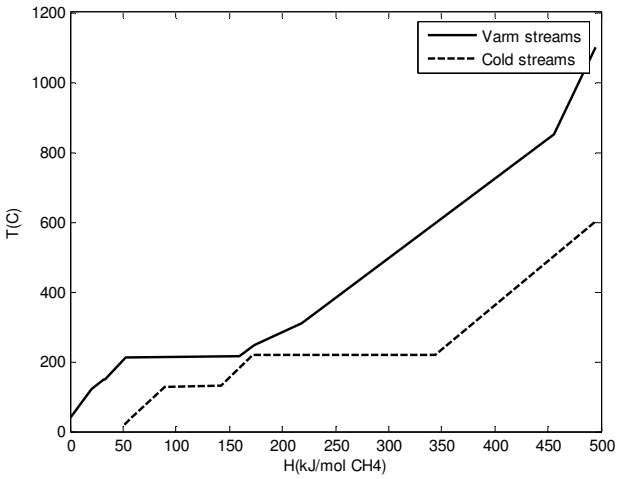


Figure 22. Composite curve for steam reforming with CO_2 capture by absorption following the water-gas shift and condenser.

Since the partial pressure of CO_2 in the synthesis gas is reasonably high, MDEA solvent should be sufficient for CO_2 capture. High purity is produced by pressure swing adsorption. This is needed or else produced H_2 would be diluted not only with CO_2, but with unconverted CH_4 as well. The efficiency of the pressure swing adsorption unit is set to a rather low value, so that the reforming furnace can be operated exclusively on H_2 rich offgas.

It is noteworthy that H_2 production by steam reforming typically is integrated with other industrial processes and configured to produce export steam. The example presented in table 1 is without steam export. Instead, much excess heat is used for steam production within the process in order to increase the H_2O/CH_4 ratio in the

feedstock. This is needed to obtain high conversion of CH_4 in the reformer tubes. Excess heat is also needed for regeneration of the absorbing solvent.

The drawback with this concept is that the CO_2 capture is limited by the presence of unconverted CH_4 in the offgas. In the example in table 1, the CO_2 capture efficiency is 88% while the weighted reformer efficiency is 73%. The capture efficiency could be increased if the efficiency of the absorption or the conversion of CH_4 in the reformer was improved. The latter could be achieved by increasing reformer temperature and increasing the H_2O/CH_4 ratio in the feedstock further.

3.4.6 Steam reforming with CO_2 capture by absorption of flue gas

Steam reforming with CO_2 capture by absorption of flue gas from the reformer furnace, which is schematically described in figure 23, is an alternative to the process presented in section 3.4.5 above.

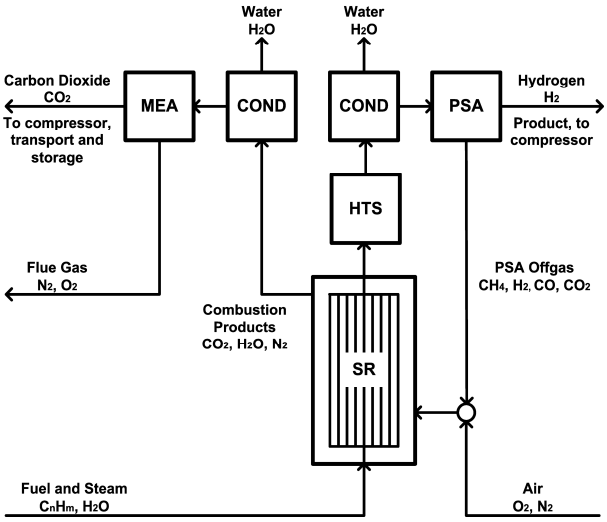


Figure 23. Schematic description of steam reforming with CO_2 capture by absorption of flue gas after the furnace.

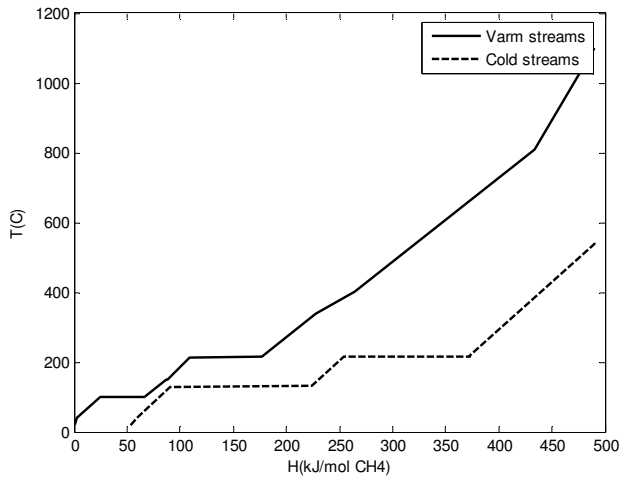


Figure 24. Composite curve for steam reforming with CO_2 capture by absorption of flue gas after the furnace.

Here CO_2 is captured in the flue gases after the reformer furnace where the CO_2 partial pressure is low. A reasonably strong absorbing solvent such as MEA and a

separate fan to overcome the pressure drop in the absorber will be needed. Excess heat is used for regeneration of the absorbing solvent. The reforming furnace is operated exclusively on offgas. In a conventional H_2 plant, high efficiency for the pressure swing adsorption would have been preferred and natural gas would have been added to the offgas before the furnace.

The advantage with this concept compared to the alternative described in section 3.4.5 is that higher CO_2 capture can be obtained, and that modest conversion of CH_4 in the reformer is acceptable. The drawback is that the efficiency penalty for regenerating the absorbing solvent is large.

The weighted reformer efficiency for the example is about 71%. This is lower than for most of the other alternatives examined. The efficiency could be increased if an absorbing solvent with less energy demand for regeneration could be used.

3.4.7 Comments on the comparative study

For many instances the process parameters used in the base cases presented in table 1 could be improved. Steam reforming at 950 ºC and preheating up to 670 ºC is commercially available, just to take an example. The comparative study presented above should be seen as a useful tool to examine strengths and weaknesses between different concepts for H_2 production with CO_2 capture.

As previously mentioned, process studies describing steam reforming with CO_2 capture by absorption in synthesis gas after water-gas shift has been made by Consonni et al [20] and Audus et al [21. In both these studies an overall efficiency of 73% with 85% CO_2 capture are reported, which is similar to the numbers for steam reforming with CO_2 capture by absorption after water-gas shift presented here.

In general, process alternatives involving pressure swing adsorption should be attractive if high purity H_2 is the wanted product. Although it would be possible, H_2 purification by pressure swing adsorption has not been considered for chemical-looping reforming. For this to be feasible, higher reactor pressure or gas compression prior to the gas separation would be needed. Additionally, there is no obvious way to utilize the pressure swing adsorption offgas within a chemical-looping reforming

process. Since the offgas would contain at least 10% of the produced H_2 this would need to be addressed in some way, for example by integration with other nearby facilities.

If the H_2 produced is to be used directly for power generation in a combined cycle, high purity H_2 would not be needed and CO_2 capture by absorption would be appropriate. As mentioned above, process studies bout power generation by reforming of natural gas to H_2 with pre-combustion CO_2 capture by absorption have been presented by Lozza and Chiesa [26, 27], Corradetti et al [23], Ertesvåg et al [24] and Undrum et al [25]. In these studies, the efficiency for power generation typically was found to be 45-49% with 88-90% CO_2 capture. These numbers should not be compared directly with those presented in table 1, where more conservative assumptions have been used and where close integration between reforming and power generation has not been considered. But since pressurized chemical-looping reforming and steam reforming with CO_2 capture by chemical-looping combustion shows considerably higher efficiency than steam reforming with CO_2 capture, it can be concluded that chemical-looping technologies should be interesting not only for H_2 production, but for power generation with pre-combustion CO_2 capture as well.

4. CONCLUSIONS

4.1 Chemical-looping reforming

As a result of the experimental work presented in paper III, it can be concluded that chemical-looping reforming of natural gas is feasible. The concept has been successfully demonstrated in a continuous laboratory reactor built up of two circulating fluidised-beds. The reactor was operating at atmospheric pressure and the temperature was 820-930 °C.

Freeze-granulated particles of $NiO/MgAl_2O_4$ were used as oxygen carrier. The particles were found to have the desired characteristics. They did not break apart or agglomerate and there was complete conversion of CH_4 and higher hydrocarbons to H_2, CO, CO_2 and H_2O.

Formation of solid carbon was identified as a potential problem. This was most apparent for reforming of dry natural gas. Adding 25 vol% steam to the natural gas reduced or even stopped the carbon formation.

From the process studies presented in paper I and section 3.4, it can be concluded that chemical-looping reforming is an interesting process concept for H_2 production with CO_2 capture. For chemical-looping reforming at atmospheric pressure, integration with a steam cycle or other nearby industrial processes would be favourable. The weighted reformer efficiency could be in the order of 74%, including CO_2 capture, CO_2 compression and H_2 compression to 20 bar. This is about the same as for steam reforming with CO_2 capture by amine absorption.

Pressurized chemical-looping reforming has even better potential. Here integration with a gas turbine would be needed or there would be a considerable energy penalty for air compression. The weighted reformer efficiency could be in the order of 81%, including CO_2 capture and CO_2 compression.

The main reasons why pressurized chemical-looping reforming has higher overall efficiency, is that it reduces the energy penalty for compression of produced H_2, and that it would make utilization of weaker absorbing solvent for CO_2 capture relatively uncomplicated.

4.2 Steam reforming with CO_2 capture by chemical-looping combustion

From the process studies presented in paper II and section 3.4, it can be concluded that integration between steam reforming and chemical-looping combustion would be a favorable method for H_2 production with CO_2 capture. Compared to conventional steam reforming, it would provide CO_2 capture without energy penalty, make it possible to increase H_2 production at the expense of export steam and eliminate formation of thermal NO_X in the reformer furnace. The weighted reformer efficiency could be in the order of 80%, including CO_2 capture and CO_2 compression. If the temperature of reforming is increased even higher efficiency would be possible.

From the reformer tube model, the preliminary reactor design and the exemplifying heat exchanger network described in paper II, it can be concluded that the concept as a whole should be feasible. Reactor dimensions, particle flows, gas flows, pressure drops, heat transfer operations and temperature levels all seem reasonable.

5. SUGGESTIONS FOR FUTURE RESEARCH

5.1 Chemical-looping reforming

There are many questions that need answers before any well-grounded conclusions about the future of chemical-looping reforming can be drawn. Firstly and foremost, a wider range of oxygen-carriers particles should be investigated. NiO seems to have many desirable properties. It is highly reactive with hydrocarbons and the selectivity towards H_2 and CO is good. But it is also known that metallic Ni catalyses carbon formation, and it was no surprise that solid carbon was observed during the experiments presented in paper III. This is not necessarily a big problem but should be further examined.

From experiments with NiO particles for chemical-looping combustion it is known that the size, inert phase and production method have impact on the oxygen-carrier properties. This will most likely be the case for chemical-looping reforming as well. Hence other inert phases than $MgAl_2O_4$ should be examined, as well as other production methods than freeze granulation.

Alternatives to NiO as active phase should also be examined. Metal oxides traditionally proposed for chemical-looping combustion such as CuO, Fe_2O_3 and Mn_3O_4 do not seem suitable, at least not according the experiments by Zafar et al [40]. But mixtures of such oxides and NiO might be functional. Small amounts of metallic Ni is likely sufficient to catalyze decomposition of CH_4, and it seems reasonable to believe that the bulk of the oxygen could as well be added with another material. Mixtures of NiO and Fe_2O_3 have been successfully tested for chemical-looping combustion by Johansson et al [53]. Another option may be CoO, which has suitable thermodynamical properties and is known to be reactive with hydrocarbon fuels. Experiments by Ishida et al [54] indicate that particles of NiO/CoO are highly reactive with CH_4 and resistant to carbon formation. Other possible active phases include CeO_2 [44-46] and mixed oxides such as $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites [47-51].

In addition to testing different oxygen-carrier particles, the effects of elevated pressure should be examined. It would also be of interest to evaluate chemical-looping

reforming in a wider range of temperatures, with different fuels and with H_2O or CO_2 added to the fuel.

Finally, it should be examined what possible advantages chemical-looping reforming could provide for other industrial processes than H_2 production, such as production of synthesis gas for methanol production and Fischer-Tropsch synthesis, where synthesis gas with a H_2/CO ratio of 2 is desired. Such synthesis gas can not be produced directly by steam reforming, but with chemical-looping reforming of natural gas it would be possible. Power generation with pre-combustion CO_2 capture by chemical-looping reforming should also be examined more closely.

5.2 Steam reforming with CO_2 capture by chemical-looping combustion

H_2 production by steam reforming and pressure swing adsorption is a well-established technology. Hence most of the components used in the process proposed in paper II are proven and commercially available. Interest should be focused on what can be considered as novel ideas.

The reformer tube model used in paper II is rather simple. The kinetics of catalytic steam reforming is fast, so the heat transfer from the fluidized bed to the reactive mixture inside the reformer tubes is the most critical model parameter. The expressions for the heat-transfer coefficient for the outside of the reformer tubes that was used in paper II is known to provide results with rather large uncertainties, see Kim et al [55]. Therefore, the first step in an improved reactor-tube model would be to examine these expressions carefully and perhaps even try to verify them experimentally.

A detailed reformer tube model would provide data with a higher degree of certainty. The reformer tube model gives the length of the fuel reactor which is a critical design parameter. If the fuel reactor becomes very long it may be necessary to provide reactor volume by increasing the height of the fluidized bed, instead of increasing the width. Otherwise the surface area of the reactor could end up so large that the pressure swing adsorption offgas becomes insufficient to obtain suitable fluidization conditions, which would require a slightly modified design approach.

The offgas from the pressure swing adsorption facility should typically consist of about 50 vol% CO_2, 25 vol % H_2, 20 vol % CH_4 and 5 vol % CO. There is no reason to believe that there would be any problems to use such gas mixture as fuel for chemical-looping combustion. In general, H_2 and CO are much more reactive than CH_4, especially if Fe_2O_3 or Mn_3O_4 are used as oxygen carrier. Still, this should be verified experimentally.

The effect of tube bundles inside the fuel reactor of a chemical-looping combustion system is not known. There is no reason to believe that it would disturb fluidization or hamper the conversion of the fuel, but erosion and corrosion of the tubes might become a problem, especially at high temperatures. This needs to be carefully considered and perhaps examined experimentally.

Finally, the option to use steam reforming with CO_2 capture by chemical-looping combustion as a method to produce H_2 for power generation with pre-combustion CO_2 capture should be examined more closely.

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8. APPENDIX

8.1 Abbreviations and subscripts

ABS = amine absorption

AC = air compression

AR = chemical looping air reactor

CLC = chemical-looping combustion

CLR = chemical-looping reforming

COMB = combustor

COMP = compressor

COND = condenser

E = power surplus/demand

FR = chemical looping fuel reactor

GT = gas turbine

H = heat surplus/demand

Hi = lower heating value

HTS = high temperature shift reactor

IPCC = Intergovernmental Panel on Climate Change

LTS = low temperature shift reactor

MDEA = absorption with methyldiethanolamine solvent

MEA = absorption with monoethanolamine solvent

n = number of moles

p = pressure or partial pressure

PSA = pressure swing adsorption

REG = solvent regeneration

SC = steam cycle

SR = steam reforming reactor

syngas = synthesis gas

T = Temperature

8.2 Chemical substances

Al_2O_3 = alumina

Ar = argon

CeO_2 = cerium oxide

CH_4 = methane

C_nH_m = generic hydrocarbon fuel

CO = carbon monoxide

CO_2 = carbon dioxide

Co/CoO = cobalt/cobalt oxide

$Cu/Cu_2O/CuO$ = cupper/cupper oxide

DEA = diethanolamine

$Fe/FeO/Fe_3O_4/Fe_2O_3$ = iron/iron oxide

H_2 = hydrogen

H_2O = water or steam

$La_{(1-x)}Sr_xFe_{(1-y)}Co_yO_{3-\delta}$ = generic LaSrFeCo perovskite

MDEA = methyldiethanolamine

MEA = monoethanolamine

Me/MeO = generic oxygen carrier

$Mn_2O_3/Mn_3O_4/MnO$ = manganese oxide

Ni/NiO = nickel/nickel oxide

N_2 = nitrogen

NO_X = nitrogen oxides

O_2 = oxygen

SO_X = sulphur oxides